

(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES  
PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG

(19) Weltorganisation für geistiges Eigentum  
Internationales Büro



(43) Internationales Veröffentlichungsdatum  
30. September 2004 (30.09.2004)

PCT

(10) Internationale Veröffentlichungsnummer  
**WO 2004/083516 A1**

(51) Internationale Patentklassifikation<sup>7</sup>: D06P 5/13, 5/02,  
D06L 3/02, C02F 1/72, C11D 3/395, 3/39

(21) Internationales Aktenzeichen: PCT/EP2004/002274

(22) Internationales Anmeldedatum:  
5. März 2004 (05.03.2004)

(25) Einreichungssprache: Deutsch

(26) Veröffentlichungssprache: Deutsch

(30) Angaben zur Priorität:  
103 11 766.0 18. März 2003 (18.03.2003) DE

(71) Anmelder (für alle Bestimmungsstaaten mit Ausnahme von  
US): BAYER CHEMICALS AG [DE/DE]; 51368 Le-  
verkusen (DE).

(72) Erfinder; und

(75) Erfinder/Anmelder (nur für US): VOGT, Uwe [DE/DE];  
Forellenweg 52, 40764 Langenfeld (DE). FRANKE, Gün-  
ter [DE/DE]; Landrat-Trimborn-Str. 60, 42799 Leichlin-  
gen (DE).

(74) Gemeinsamer Vertreter: BAYER CHEMICALS AG;  
Law & Patents, Patents and Licensing, 51368 Leverkusen  
(DE).

(81) Bestimmungsstaaten (soweit nicht anders angegeben, für  
jede verfügbare nationale Schutzrechtsart): AE, AG, AL,  
AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH,  
CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES,  
FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE,  
KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD,  
MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG,  
PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM,  
TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM,  
ZW.

(84) Bestimmungsstaaten (soweit nicht anders angegeben, für  
jede verfügbare regionale Schutzrechtsart): ARIPO (BW,  
GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM,  
ZW), eurasisches (AM, AZ, BY, KG, KZ, MD, RU, TJ,  
TM), europäisches (AT, BE, BG, CH, CY, CZ, DE, DK,  
EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT,  
RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA,  
GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Veröffentlicht:

— mit internationalem Recherchenbericht

Zur Erklärung der Zweibuchstaben-Codes und der anderen Ab-  
kürzungen wird auf die Erklärungen ("Guidance Notes on Co-  
des and Abbreviations") am Anfang jeder regulären Ausgabe der  
PCT-Gazette verwiesen.

(54) Title: OXIDATION SYSTEM CONTAINING A MACROCYCLIC METAL COMPLEX, THE PRODUCTION THEREOF  
AND ITS USE

(54) Bezeichnung: OXIDATIONSSYSTEM ENTHALTEND EINEN MAKROCYCLISCHEN METALLKOMPLEX, DESSEN  
HERSTELLUNG UND VERWENDUNG

(57) Abstract: The invention relates to an oxidation system containing a macrocyclic metal complex, an oxidizing agent and an  
oxidation-increasing compound. This oxidation system is suited for use under diverse reaction conditions for oxidizing oxidizable  
substances by brining the oxidizable substance into contact with the special oxidation system. It is possible to use this oxidation  
system, for example, in a method for removing excess unbound dye from textile materials after a dying process.

(57) Zusammenfassung: Bereitgestellt wird Oxidationssystem enthaltend einen makrocyclischen Metallkomplex, ein Oxidations-  
mittel und eine oxidationsverstärkende Verbindung. Dieses Oxidationssystem eignet sich unter vielfältigen Reaktionsbedingungen  
zur Oxidation von oxidierbaren Substanzen, indem man die oxidierbare Substanz mit dem speziellen Oxidationssystem in Kontakt  
bringt. Möglich ist beispielsweise der Einsatz in einem Verfahren zur Entfernung überschüssigen, nichtgebundenen Farbstoffs von  
textilen Materialien nach einer Färbung.

BEST AVAILABLE COPY

Oxidation system containing a macrocyclic metal complex, the production thereof and its use

JC20 Rec'd PCT/PTO 01 SEP 2005

5 The present invention relates to an oxidizing system comprising a macrocyclic metal complex, an oxidizing agent and an oxidation-enhancing compound and also a process for oxidizing oxidizable substances by contacting the oxidizable substance with the specific oxidizing system.

10 EP-A-0 918 840, US-A-6,099,586 and WO-A-02/16330 disclose specific macrocyclic metal complexes useful as bleach activators. Combined with a peroxide source, preferably hydrogen peroxide, these bleach activators make it possible to carry out oxidation reactions. Such oxidation reactions are carried out for example in paper bleaching, in the decolorization of colored wastewaters or in the desulfurization of motor fuels. The use in household laundry detergents for  
15 respectively removing and decolorizing soil on the laundry and in the wash liquor is also described. In all these applications, the use of the specific macrocyclic metal complexes leads to an improvement in the results compared with the sole treatment just with a peroxide source.

20 Owing to the multiplicity of possible oxidation reactions, there is an interest in providing improved oxidizing systems which can be as widely used as possible.

It has now been found that, surprisingly, the addition of specific oxidation-enhancing compounds to a macrocyclic metal complex and an oxidizing agent quite  
25 unexpectedly provides a distinct improvement in oxidizing performance.

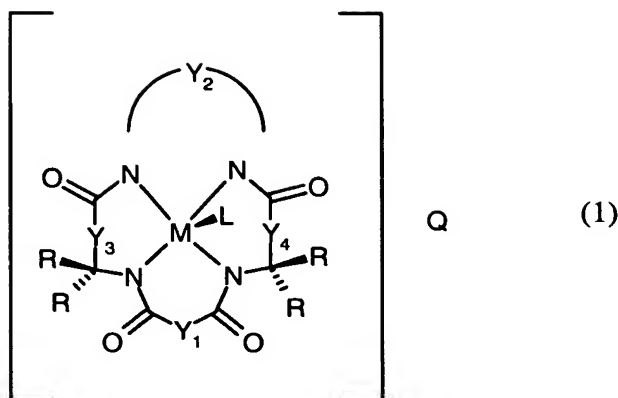
The invention accordingly provides an oxidizing system comprising the three components

30 1) a macrocyclic metal complex of the general formula (I)

"Express Mail" mailing label number EV 685752035 US  
Date of Deposit September 1, 2005

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Commissioner of Patents and Trademarks, Alexandria, VA 22313-1450

Bill Denenrich  
(Name of person mailing paper or fee)  
Signature of person mailing paper or fee)



where

5  $Y_1$ ,  $Y_3$  and  $Y_4$  are each independently a single bond or a bridge member which contains 1, 2 or 3 carbon atoms in the bridge,

$Y_2$  is a bridge member having at least 1 carbon atom in the bridge,

10  $R$  is independently in each occurrence hydrogen, alkyl, cycloalkyl, cycloalkenyl, alkenyl, aryl, alkynyl, alkylaryl, halogen, alkoxy, phenoxy,  $CH_2CF_3$  or  $CF_3$  or two  $R$  radicals which are bound to the same carbon atom combine to form a substituted or unsubstituted benzene, cycloalkyl or cycloalkenyl ring, the carbon atom to which the two  $R$  radicals are bound being part of the benzene, cycloalkyl or cycloalkenyl ring,

15  $M$  is a transition metal in the oxidation states I, II, III, IV, V or VI or is selected from groups 6, 7, 8, 9, 10 and 11 of the periodic table,

20  $Q$  is a counterion which balances the charge of the macrocyclic metal complex on a stoichiometric basis, and

$L$  is a further ligand.

25 2) an oxidizing agent, and

3) an oxidation-enhancing compound.

Preferably in the general formula (1)

Y<sub>1</sub>, Y<sub>3</sub> and Y<sub>4</sub> are each independently a (-CH<sub>2</sub>-)<sub>x</sub> group, where x is 1, 2 or 3 and one or more hydrogen atoms in the (-CH<sub>2</sub>-)<sub>x</sub> group may be substituted by an R<sup>i</sup> radical, R<sup>i</sup> being alkyl, cycloalkyl, cycloalkenyl, alkenyl, aryl, alkynyl, alkylaryl, halogen, alkoxy or phenoxy, or two R<sup>i</sup> radicals which are bound to two adjacent carbon atoms of the (-CH<sub>2</sub>-)<sub>x</sub> group combine to form a benzene, cycloalkyl or cycloalkenyl ring which may contain one or more hetero atoms, preferably oxygen, sulfur or nitrogen.

Preferably in the general formula (1), Y<sub>2</sub> is

a bridge member having 1, 2 or 3 carbon atoms in the bridge, preferably a (-CH<sub>2</sub>-)<sub>y</sub> group, where y is 1 or 2 and one or more hydrogen atoms in the (-CH<sub>2</sub>-)<sub>x</sub> group may be substituted by an R<sup>ii</sup> radical, R<sup>ii</sup> being alkyl, cycloalkyl, cycloalkenyl, alkenyl, aryl, alkynyl, alkylaryl, halogen, alkoxy or phenoxy, or two R<sup>ii</sup> radicals which are bound to two adjacent carbon atoms of the (-CH<sub>2</sub>-)<sub>x</sub> group combine to form an optionally substituted benzene, cycloalkyl or cycloalkenyl ring which may contain one or more hetero atoms, preferably oxygen, sulfur or nitrogen, preferably a benzene ring which may be substituted by electron-donating or electron-withdrawing radicals.

Preferably in the general formula (1) the R radicals are each independently hydrogen, C<sub>1</sub>-C<sub>8</sub>-alkyl, C<sub>3</sub>-C<sub>8</sub>-cycloalkyl, C<sub>4</sub>-C<sub>12</sub>-cycloalkenyl, C<sub>2</sub>-C<sub>8</sub>-alkenyl, C<sub>6</sub>-C<sub>14</sub>-aryl, C<sub>2</sub>-C<sub>12</sub>-alkynyl, C<sub>1</sub>-C<sub>12</sub>-alkylaryl, halogen, alkoxy, phenoxy, CH<sub>2</sub>CF<sub>3</sub> or CF<sub>3</sub> or two R radicals which are bound to the same carbon atom combine to form a substituted or unsubstituted benzene, C<sub>3</sub>-C<sub>8</sub>-cycloalkyl or C<sub>4</sub>-C<sub>12</sub>-cycloalkenyl ring, the carbon atom to which the two R radicals are bound being part of the benzene, cycloalkyl or cycloalkenyl ring.

The M metal in the general formula (1) represents a transition metal having the oxidation states I, II, III, IV, V or VI or is selected from groups 6, 7, 8, 9, 10 or 11 of the periodic table. Preferably the M metal represents Cr, Mo, W, Mn, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd and/or Pt. Mixtures of metals of the aforementioned oxidation states or  
5 from the identified groups of the periodic table are likewise possible.

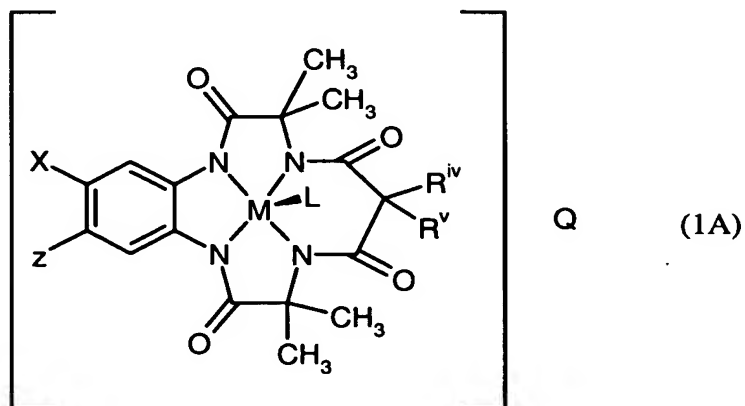
In the general formula (1) Q is a counterion which balances the charge of the macrocyclic metal complex on a stoichiometric basis. The metal-ligand complex is typically negative, preferably -1. Consequently, the counterion generally has a  
10 positive charge and given a preferred negative charge of -1 is accordingly +1.

Suitably, Q is an alkali metal counterion, preferably potassium, lithium or sodium,  $\text{NR}^{\text{iii}}_4^+$  or  $\text{PR}^{\text{iii}}_4^+$ , where every  $\text{R}^{\text{iii}}$  may independently be hydrogen, alkyl, aryl, alkylaryl, alkenyl or joins to form a cycloalkyl, cycloalkenyl or an aryl ring which  
15 optionally contains one or more hetero atoms, preferably oxygen, sulfur or nitrogen.

L is any further ligand which can attach to M. Preferably, L is a labile ligand, especially  $\text{H}_2\text{O}$ , Cl or CN.

20 The aforementioned preferred and particularly preferred meanings for  $\text{Y}_1\text{-Y}_4$ ,  $\text{R}$ ,  $\text{R}^{\text{i}}$ ,  $\text{R}^{\text{ii}}$ ,  $\text{R}^{\text{iii}}$ , Q and L may be combined in any desired manner.

The oxidizing system of the present invention preferably utilizes macrocyclic metal complexes of the general formula (1A)



25

where

- X and Z are each independently hydrogen, electron-donating or electron-withdrawing groups,
- 5 R<sup>iv</sup> and R<sup>v</sup> are each independently hydrogen, alkyl, cycloalkyl, cycloalkenyl, alkenyl, aryl, alkynyl, alkylaryl, halogen, alkoxy or phenoxy radicals or combine to form a cycloalkyl or cycloalkenyl ring which may contain one or more hetero atoms,
- 10 M is a transition metal of the oxidation states I, II, III, IV, V or VI or is selected from groups 6, 7, 8, 9, 10 or 11 of the periodic table,
- Q is a counterion which balances the charge of the macrocyclic metal complex on a stoichiometric basis, and
- 15 L is a further ligand.

In the macrocyclic metal complex of the formula (IA) X and Z may each be independently hydrogen or electron-donating or electron-withdrawing radicals. Electron-donating or electron-withdrawing radicals change the electron density of the metal-ligand complex and thus influence its reactivity.

20

Suitable electron-withdrawing radicals are for example halogens, preferably chlorine, bromine or iodine, more preferably chlorine, SO<sub>3</sub><sup>-</sup>, OSO<sub>3</sub><sup>-</sup>, OSO<sub>3</sub>R<sup>vi</sup> (where R<sup>vi</sup> is hydrogen, alkyl, aryl or alkylaryl) or NO<sub>2</sub><sup>-</sup>.

25

Suitable electron-donating radicals are for example C<sub>1</sub>-C<sub>8</sub>-alkoxy, preferably methoxy, ethoxy, propoxy and butoxy, C<sub>1</sub>-C<sub>8</sub>-alkyl, preferably methyl, ethyl, propyl, n-butyl and tert-butyl, and hydrogen.

30 In the macrocyclic metal complex of the formula (1A) R<sup>iv</sup> and R<sup>v</sup> are each independently hydrogen, alkyl, cycloalkyl, cycloalkenyl, alkenyl, aryl, alkynyl, halogen, alkoxy or phenoxy radicals. R<sup>iv</sup> and R<sup>v</sup> are preferably each independently alkyl, particularly preferably C<sub>1</sub>-C<sub>5</sub>-alkyl. More preferably R<sup>iv</sup> and R<sup>v</sup> are both identically methyl or ethyl. Even more preferably, R<sup>iv</sup> and R<sup>v</sup> combine to form a

cycloalkyl ring, especially a cyclopentyl or cyclohexyl ring, or a cycloalkenyl ring. This cycloalkyl or cycloalkenyl ring may contain one or more hetero atoms, preferably oxygen, sulfur or nitrogen.

- 5 The preparation of the macrocyclic metal complexes present in the inventive oxidizing system is described in EP-A-918 840, US-A-6,099,586 and WO-A-02/16330, each of which is hereby explicitly incorporated herein by reference.

10 The oxidizing agent can be any organic or inorganic oxidizing agent. A peroxy compound is typically used. Suitable peroxy compounds are hydrogen peroxide, hydrogen peroxide adducts, compounds capable of releasing or generating hydrogen peroxide in aqueous solution, organic peroxides, persulfates, perphosphates and persilicates.

- 15 Hydrogen peroxide adducts include alkali metal, preferably sodium, lithium or potassium, carbonate peroxyhydrate and also urea peroxide.

20 Compounds capable of generating hydrogen peroxide in aqueous solution include alkali metal, preferably sodium, potassium or lithium, perborate (as mono- or tetrahydrate). Such perborates are commercially available.

Alternatively, an alcohol oxidase and its appropriate alcohol substrate can be used as peroxide source.

- 25 Organic peroxides include benzoyl and cumene hydroperoxides.

Persulfates include peroxymonosulfate and Caro's acid.

Particularly preferred oxidizing agents are hydrogen peroxide and sodium perborate.

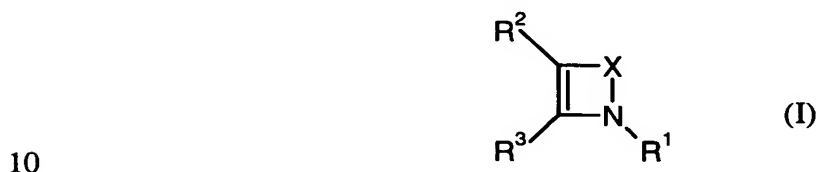
30

The oxidation-enhancing compounds ("mediator") are aliphatic, cycloaliphatic, heterocyclic or aromatic compounds having at least one OH, NO, NOH, HRN-OH functionality or mixtures thereof.

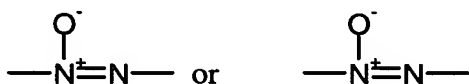
Such compounds and their preparation are described in EP-A-0 885 868, WO-A-97/06244 and WO-A-96/12845.

5 Examples of such compounds are the hereinbelow identified compounds of the formula (I), (II), (III) and (IV), the compounds of the formulae (II), (III) and (IV) being preferred and the compounds of the formulae (III) and (IV) being particularly preferred.

Compounds of the general formula (I) are:



where X represents  $(-N=N-)$ ,  $(-N=CR^4-)_p$ ,  $(-CR^4=N-)_p$ ,  $(-CR^5=CR^6)_p$ ,



15

and p is 1 or 2,

20 where the radicals  $R^1$  to  $R^6$  be the same or different and may each independently denote: hydrogen, halogen, hydroxyl, formyl, carboxyl and also salts and esters thereof, amino, nitro,  $C_1$ - $C_{12}$ -alkyl,  $C_1$ - $C_6$ -alkyloxy, carbonyl- $C_1$ - $C_6$ -alkyl, phenyl, sulfo and also esters and salts thereof, sulfamoyl, carbamoyl, phospho, phosphono, phosphonooxy and also salts and esters thereof, where the amino, carbamoyl and sulfamoyl groups of the radicals  $R^1$  to  $R^6$  may be unsubstituted or singly or doubly hydroxyl,  $C_1$ - $C_3$ -alkyl or  $C_1$ - $C_3$ -alkoxy substituted, and where the radicals  $R^2$  and  $R^3$  may combine to form a conjoint group -A- and -A- is  $(-CR^7=CR^8-CR^9=CR^{10}-)$  or  $(-CR^{10}=CR^9-CR^8=CR^7-)$ .

25

The radicals  $R^7$  to  $R^{10}$  may be the same or different and each independently denote: hydrogen, halogen, hydroxyl, formyl, carboxyl and also salts and esters thereof, amino, nitro,  $C_1$ - $C_{12}$ -alkyl,  $C_1$ - $C_6$ -alkyloxy, carbonyl- $C_1$ - $C_5$ -alkyl, phenyl, aryl, sulfo

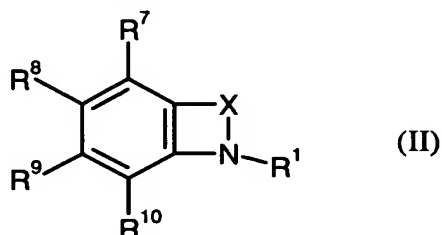
30

and also esters and salts thereof, sulfamoyl, carbamoyl, phospho, phosphono, phosphonooxy and also salts and esters thereof, where the amino, carbamoyl and sulfamoyl groups of the radicals  $R^7$  to  $R^{10}$  may be unsubstituted or singly or doubly hydroxyl,  $C_1$ - $C_3$ -alkyl or  $C_1$ - $C_3$ -alkoxy substituted, and where the  $C_1$ - $C_{12}$ -alkyl,  $C_1$ - $C_6$ -alkyloxy, carbonyl- $C_1$ - $C_6$ -alkyl, phenyl and aryl groups of the radicals  $R^7$  to  $R^{10}$  may be unsubstituted or singly or multiply  $R^{11}$  substituted and where  $R^{11}$  denotes one of the following groups: hydrogen, halogen, hydroxyl, formyl, carboxyl and also salts and esters thereof, amino, nitro,  $C_1$ - $C_{12}$ -alkyl,  $C_1$ - $C_6$ -alkyloxy, carbonyl- $C_1$ - $C_6$ -alkyl, phenyl, aryl, sulfo and also esters and salts thereof, where the carbamoyl, sulfamoyl and amino groups of the  $R^{11}$  radical may be unsubstituted or singly or doubly  $R^{12}$  substituted and  $R^{12}$  may denote one of the following groups: hydrogen, hydroxyl, formyl, carboxyl and also salts and esters thereof, amino, nitro,  $C_1$ - $C_{12}$ -alkyl,  $C_1$ - $C_6$ -alkyloxy, carbonyl- $C_1$ - $C_6$ -alkyl, phenyl or aryl.

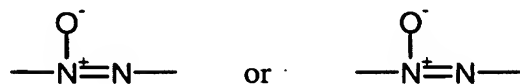
Examples of the identified compounds of the general formula (I) are:

- 1-hydroxy-1,2,3-triazole-4,5-dicarboxylic acid
- 1-phenyl-1H-1,2,3-triazole 3-oxide
- 5-chloro-1-phenyl-1H-1,2,3-triazole 3-oxide
- 5-methyl-1-phenyl-1H-1,2,3-triazole 3-oxide
- 4-(2,2-dimethylpropanoyl)-1-hydroxy-1H-1,2,3-triazole
- 4-hydroxy-2-phenyl-2H-1,2,3-triazole 1-oxide
- 2,4,5-triphenyl-2H-1,2,3-triazole 1-oxide
- 1-benzyl-1H-1,2,3-triazole 3-oxide
- 1-benzyl-4-chloro-1H-1,2,3-triazole 3-oxide
- 1-benzyl-4-bromo-1H-1,2,3-triazole 3-oxide
- 1-benzyl-4-methoxy-1H-1,2,3-triazole 3-oxide

Compounds of the general formula (II) are:



where X represents  $(-N=N-)$ ,  $(-N=CR^4-)_p$ ,  $(-CR^4=N-)_p$ ,  $(-CR^5=CR^6)_p$ ,



5 and p is 1 or 2.

The radicals  $R^1$  and  $R^4$  to  $R^{10}$  may be the same or different and denote one of the following groups: hydrogen, halogen, hydroxyl, formyl, carboxyl and also salts and esters thereof, amino, nitro,  $C_1$ - $C_{12}$ -alkyl,  $C_1$ - $C_5$ -alkyloxy, carbonyl- $C_1$ - $C_6$ -alkyl, phenyl, aryl, sulfo and also esters and salts thereof, sulfamoyl, carbamoyl, phospho, phosphono, phosphonooxy and also salts and esters thereof, where the amino, carbamoyl and sulfamoyl groups of the radicals  $R^1$  and  $R^4$  to  $R^{10}$  may also be unsubstituted or singly or doubly hydroxyl,  $C_1$ - $C_3$ -alkyl or  $C_1$ - $C_3$ -alkoxy substituted and where the  $C_1$ - $C_{12}$ -alkyl,  $C_1$ - $C_6$ -alkyloxy, carbonyl- $C_1$ - $C_6$ -alkyl, phenyl, aryl and aryl- $C_1$ - $C_6$ -alkyl groups of the radicals  $R^1$  and  $R^4$  to  $R^{10}$  may be unsubstituted or singly or multiply  $R^{12}$  substituted and where  $R^{12}$  may denote: hydrogen, halogen, hydroxyl, formyl, carboxyl and also salts and esters thereof, amino, nitro,  $C_1$ - $C_{12}$ -alkyl,  $C_1$ - $C_6$ -alkyloxy, carbonyl- $C_1$ - $C_6$ -alkyl, phenyl, aryl, sulfo, sulfeno, sulfino and also esters and salts thereof, where the carbamoyl, sulfamoyl and amino groups of the  $R^{12}$  radical may be unsubstituted or singly or doubly  $R^{13}$  substituted and where  $R^{13}$  may denote one of the following groups: hydrogen, hydroxyl, formyl, carboxyl and also salts and esters thereof, amino, nitro,  $C_1$ - $C_{12}$ -alkyl,  $C_1$ - $C_6$ -alkyloxy, carbonyl- $C_1$ - $C_6$ -alkyl, phenyl or aryl.

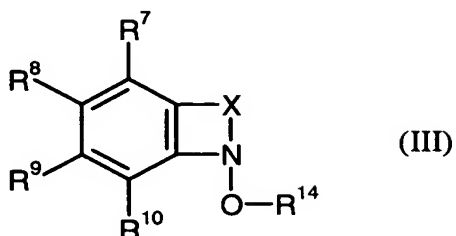
25 Examples of the identified compounds of the general formula (II) are:

### 1-Hydroxybenzimidazoles

- 1-Hydroxybenzimidazole-2-carboxylic acid
- 1-Hydroxybenzimidazole
- 2-Methyl-1-hydroxybenzimidazole
- 2-Phenyl-1-hydroxybenzimidazole

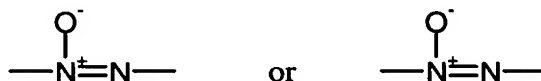
**1-Hydroxyindoles****2-Phenyl-1-hydroxyindole**

5 Substances of the general formula (III) are:



where X represents  $(-N=N-)$ ,  $(-N=CR^4-)_m$ ,  $(-CR^4=N-)_m$ ,  $(-CR^5=CR^6-)_m$ ,

10



and m is 1 or 2.

15 The radicals  $R^7$  to  $R^{10}$  and  $R^4$  to  $R^6$  are each subject to the above remarks.

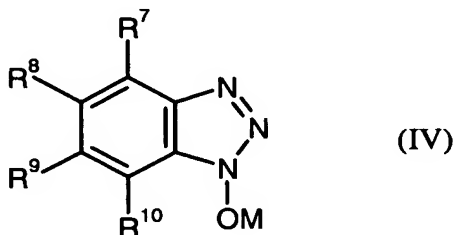
$R^{14}$  may denote:  $-M$ , where M denotes hydrogen, alkali, preferably lithium, sodium or potassium, alkaline earth, preferably calcium or magnesium, ammonium,  $C_1$ - $C_4$ -alkylammonium or  $C_1$ - $C_4$ -alkanolammonium,  $C_1$ - $C_{10}$ -alkyl,  $C_1$ - $C_{10}$ -alkylcarbonyl,

20 where  $C_1$ - $C_{10}$ -alkyl and  $C_1$ - $C_{10}$ -alkylcarbonyl may be unsubstituted or singly or multiply  $R^{15}$  substituted, where  $R^{15}$  may denote one of the following groups:

hydrogen, halogen, hydroxyl, formyl, carboxyl and also salts and esters thereof, amino, nitro,  $C_1$ - $C_{12}$ -alkyl,  $C_1$ - $C_6$ -alkyloxy, carbonyl- $C_1$ - $C_6$ -alkyl, phenyl, sulfo, and also esters and salts thereof, sulfamoyl, carbamoyl, phospho, phosphono,

25 phosphonooxy and also salts and esters thereof, where the amino, carbamoyl and sulfamoyl groups of the  $R^{15}$  radical may be unsubstituted or singly or doubly hydroxyl,  $C_1$ - $C_3$ -alkyl or  $C_1$ - $C_3$ -alkoxy substituted.

Of the substances of the formula (III) it is in particular derivatives of 1-hydroxybenzotriazole and of the tautomeric benzotriazole 1-oxide and also esters and salts thereof which are preferred (compounds of the formula (IV))



5

where

M denotes hydrogen, alkali, preferably lithium, sodium or potassium, alkaline earth, preferably calcium or magnesium, ammonium, C<sub>1</sub>-C<sub>4</sub>-alkylammonium or C<sub>1</sub>-C<sub>4</sub>-alkanolammonium.

The radicals R<sup>7</sup> to R<sup>10</sup> may be the same or different and each independently denote one of the following groups: hydrogen, halogen, hydroxyl, formyl, carboxyl and also salts and esters thereof, amino, nitro, C<sub>1</sub>-C<sub>12</sub>-alkyl, C<sub>1</sub>-C<sub>6</sub>-alkyloxy, carbonyl-C<sub>1</sub>-C<sub>6</sub>-alkyl, phenyl, sulfo and also esters and salts thereof, sulfamoyl, carbamoyl, phospho, phosphono, phosphonooxy and also salts and esters thereof, where the amino, carbamoyl and sulfamoyl groups of the radicals R<sup>7</sup> to R<sup>10</sup> may be unsubstituted or singly or doubly hydroxyl, C<sub>1</sub>-C<sub>3</sub>-alkyl or C<sub>1</sub>-C<sub>3</sub>-alkoxy substituted, and where the C<sub>1</sub>-C<sub>12</sub>-alkyl, C<sub>1</sub>-C<sub>6</sub>-alkyloxy, carbonyl-C<sub>1</sub>-C<sub>5</sub>-alkyl, phenyl and aryl groups of the radicals R<sup>7</sup> to R<sup>10</sup> may be unsubstituted or singly or multiply R<sup>16</sup> substituted and where R<sup>16</sup> may denote one of the following groups: hydrogen, halogen, hydroxyl, formyl, carboxyl and also salts and esters thereof, amino, nitro, C<sub>1</sub>-C<sub>12</sub>-alkyl, C<sub>1</sub>-C<sub>6</sub>-alkyloxy, carbonyl-C<sub>1</sub>-C<sub>6</sub>-alkyl, phenyl, aryl, sulfo, sulfeno, sulfinio and also esters and salts thereof, where the carbamoyl, sulfamoyl and amino groups of the R<sup>16</sup> radical may be unsubstituted or singly or doubly R<sup>17</sup> substituted and R<sup>17</sup> may denote one of the following groups: hydrogen, hydroxyl, formyl, carboxyl and also salts and esters thereof, amino, nitro, C<sub>1</sub>-C<sub>12</sub>-alkyl, C<sub>1</sub>-C<sub>6</sub>-alkyloxy, carbonyl-C<sub>1</sub>-C<sub>6</sub>-alkyl, phenyl or aryl.

30 Examples of the identified compounds of the general formula (III) are:

**1-Hydroxybenzotriazoles**

	1-Hydroxybenzotriazole
	1-Hydroxybenzotriazole, sodium salt
5	1-Hydroxybenzotriazole, potassium salt
	1-Hydroxybenzotriazole, lithium salt
	1-Hydroxybenzotriazole, ammonium salt
	1-Hydroxybenzotriazole, calcium salt
	1-Hydroxybenzotriazole, magnesium salt
10	1-Hydroxybenzotriazole-4-sulfonic acid
	1-Hydroxybenzotriazole-4-sulfonic acid, sodium salt
	1-Hydroxybenzotriazole-4-sulfonic acid, potassium salt
	1-Hydroxybenzotriazole-4-sulfonic acid, ammonium salt
	1-Hydroxybenzotriazole-5-sulfonic acid
15	1-Hydroxybenzotriazole-5-sulfonic acid, sodium salt
	1-Hydroxybenzotriazole-5-sulfonic acid, potassium salt
	1-Hydroxybenzotriazole-5-sulfonic acid, ammonium salt
	1-Hydroxybenzotriazole-6-sulfonic acid
	1-Hydroxybenzotriazole-6-sulfonic acid, sodium salt
20	1-Hydroxybenzotriazole-6-sulfonic acid, potassium salt
	1-Hydroxybenzotriazole-6-sulfonic acid, ammonium salt
	1-Hydroxybenzotriazole-7-sulfonic acid
	1-Hydroxybenzotriazole-7-sulfonic acid, sodium salt
	1-Hydroxybenzotriazole-7-sulfonic acid, potassium salt
25	1-Hydroxybenzotriazole-7-sulfonic acid, ammonium salt
	1-Hydroxybenzotriazole-6-sulfonic acid, monosodium salt
	1-Hydroxybenzotriazole-4-carboxylic acid
	1-Hydroxybenzotriazole-4-carboxylic acid, sodium salt
	1-Hydroxybenzotriazole-4-carboxylic acid, potassium salt
30	1-Hydroxybenzotriazole-4-carboxylic acid, ammonium salt
	1-Hydroxybenzotriazole-5-carboxylic acid
	1-Hydroxybenzotriazole-5-carboxylic acid, sodium salt
	1-Hydroxybenzotriazole-5-carboxylic acid, potassium salt
	1-Hydroxybenzotriazole-5-carboxylic acid, ammonium salt

- 1-Hydroxybenzotriazole-6-carboxylic acid  
1-Hydroxybenzotriazole-6-carboxylic acid, sodium salt  
1-Hydroxybenzotriazole-6-carboxylic acid, potassium salt  
1-Hydroxybenzotriazole-6-carboxylic acid, ammonium salt
- 5 1-Hydroxybenzotriazole-7-carboxylic acid  
1-Hydroxybenzotriazole-7-carboxylic acid, sodium salt  
1-Hydroxybenzotriazole-7-carboxylic acid, potassium salt  
1-Hydroxybenzotriazole-7-carboxylic acid, ammonium salt  
1-Hydroxybenzotriazole-6-N-phenylcarboxamide
- 10 5-Ethoxy-6-nitro-1-hydroxybenzotriazole  
4-Ethyl-7-methyl-6-nitro-1-hydroxybenzotriazole  
2,3-Bis-(4-ethoxy-phenyl)-4,6-dinitro-2,3-dihydro-1-hydroxybenzotriazole  
2,3-Bis-(2-bromo-4-methyl-phenyl)-4,6-dinitro-2,3-dihydro-1-hydroxybenzotriazole
- 15 2,3-Bis-(4-bromo-phenyl)-4,6-dinitro-2,3-dihydro-1-hydroxybenzotriazole  
2,3-Bis-(4-carboxy-phenyl)-4,6-dinitro-2,3-dihydro-1-hydroxybenzotriazole  
4,6-Bis-(trifluoromethyl)-1-hydroxybenzotriazole  
5-Bromo-1-hydroxybenzotriazole  
6-Bromo-1-hydroxybenzotriazole
- 20 4-Bromo-7-methyl-1-hydroxybenzotriazole  
5-Bromo-7-methyl-6-nitro-1-hydroxybenzotriazole  
4-Bromo-6-nitro-1-hydroxybenzotriazole  
6-Bromo-4-nitro-1-hydroxybenzotriazole  
4-Chloro-1-hydroxybenzotriazole
- 25 5-Chloro-1-hydroxybenzotriazole  
6-Chloro-1-hydroxybenzotriazole  
6-Chloro-5-isopropyl-1-hydroxybenzotriazole  
5-Chloro-6-methyl-1-hydroxybenzotriazole  
6-Chloro-5-methyl-1-hydroxybenzotriazole
- 30 4-Chloro-7-methyl-6-nitro-1-hydroxybenzotriazole  
4-Chloro-5-methyl-1-hydroxybenzotriazole  
5-Chloro-4-methyl-1-hydroxybenzotriazole  
4-Chloro-6-nitro-1-hydroxybenzotriazole  
6-Chloro-4-nitro-1-hydroxybenzotriazole

- 7-Chloro-1-hydroxybenzotriazole  
6-Diacetylamino-1-hydroxybenzotriazole  
2,3-Dibenzyl-4,6-dinitro-2,3-dihydro-1-hydroxybenzotriazole  
4,6-Dibromo-1-hydroxybenzotriazole  
5 4,6-Dichloro-1-hydroxybenzotriazole  
5,6-Dichloro-1-hydroxybenzotriazole  
4,5-Dichloro-1-hydroxybenzotriazole  
4,7-Dichloro-1-hydroxybenzotriazole  
5,7-Dichloro-6-nitro-1-hydroxybenzotriazole  
10 5,6-Dimethoxy-1-hydroxybenzotriazole  
2,3-Di-[2]naphthyl-4,6-dinitro-2,3-dihydro-1-hydroxybenzotriazole  
4,6-Dinitro-1-hydroxybenzotriazole  
4,6-Dinitro-2,3-diphenyl-2,3-dihydro-1-hydroxybenzotriazole  
4,6-Dinitro-2,3-di-p-tolyl-2,3-dihydro-1-hydroxybenzotriazole  
15 5-Hydrazino-7-methyl-4-nitro-1-hydroxybenzotriazole  
5,6-Dimethyl-1-hydroxybenzotriazole  
4-Methyl-1-hydroxybenzotriazole  
5-Methyl-1-hydroxybenzotriazole  
6-Methyl-1-hydroxybenzotriazole  
20 5-(1-Methylethyl)-1-hydroxybenzotriazole  
4-Methyl-6-nitro-1-hydroxybenzotriazole  
6-Methyl-4-nitro-1-hydroxybenzotriazole  
5-Methoxy-1-hydroxybenzotriazole  
6-Methoxy-1-hydroxybenzotriazole  
25 7-Methyl-6-nitro-1-hydroxybenzotriazole  
4-Nitro-1-hydroxybenzotriazole  
6-Nitro-1-hydroxybenzotriazole  
6-Nitro-4-phenyl-1-hydroxybenzotriazole  
5-Phenylmethyl-1-hydroxybenzotriazole  
30 4-Trifluoromethyl-1-hydroxybenzotriazole  
5-Trifluoromethyl-1-hydroxybenzotriazole  
6-Trifluoromethyl-1-hydroxybenzotriazole  
4,5,6,7-Tetrachloro-1-hydroxybenzotriazole  
4,5,6,7-Tetrafluoro-1-hydroxybenzotriazole

- 6-Tetrafluoroethyl-1-hydroxybenzotriazole
- 4,5,6-Trichloro-1-hydroxybenzotriazole
- 4,6,7-Trichloro-1-hydroxybenzotriazole
- 6-Sulfamido-1-hydroxybenzotriazole
- 5 6-N,N-Diethyl-sulfamido-1-hydroxybenzotriazole
- 6-N-Methylsulfamido-1-hydroxybenzotriazole
- 6-(1H-1,2,4-Triazol-1-ylmethyl)-1-hydroxybenzotriazole
- 6-(5,6,7,8-Tetrahydroimidazo-[1,5-a]-pyridin-5-yl)-1-hydroxybenzotriazole
- 6-(Phenyl-1H-1,2,4-triazol-1-ylmethyl)-1-hydroxybenzotriazole
- 10 6-[(5-Methyl-1H-imidazo-1-yl)-phenylmethyl]-1-hydroxybenzotriazole
- 6-[(4-Methyl-1H-imidazo-1-yl)-phenylmethyl]-1-hydroxybenzotriazole
- 6-[(2-Methyl-1H-imidazo-1-yl)-phenylmethyl]-1-hydroxybenzotriazole
- 6-(1H-Imidazol-1-yl-phenylmethyl)-1-hydroxybenzotriazole
- 5-(1H-Imidazol-1-yl-phenylmethyl)-1-hydroxybenzotriazole
- 15 6-[1-(1H-Imidazol-1-yl)-ethyl]-1-hydroxybenzotriazole monohydrochloride

### 3H-Benzotriazole 1-oxides

- 3H-Benzotriazole 1-oxide
- 6-Acetyl-3H-benzotriazole 1-oxide
- 20 5-Ethoxy-6-nitro-3H-benzotriazole 1-oxide
- 4-Ethyl-7-methyl-6-nitro-3H-benzotriazole 1-oxide
- 6-Amino-3,5-dimethyl-3H-benzotriazole 1-oxide
- 6-Amino-3-methyl-3H-benzotriazole 1-oxide
- 5-Bromo-3H-benzotriazole 1-oxide
- 25 6-Bromo-3H-benzotriazole 1-oxide
- 4-Bromo-7-methyl-3H-benzotriazole 1-oxide
- 5-Bromo-4-chloro-6-nitro-3H-benzotriazole 1-oxide
- 4-Bromo-6-nitro-3H-benzotriazole 1-oxide
- 6-Bromo-4-nitro-3H-benzotriazole 1-oxide
- 30 5-Chloro-3H-benzotriazole 1-oxide
- 6-Chloro-3H-benzotriazole 1-oxide
- 4-Chloro-6-nitro-3H-benzotriazole 1-oxide
- 4,6-Dibromo-3H-benzotriazole 1-oxide
- 4,6-Dibromo-3-methyl-3H-benzotriazole 1-oxide

- 4,6-Dichloro-3H-benzotriazole 1-oxide  
4,7-Dichloro-3H-benzotriazole 1-oxide  
5,6-Dichloro-3H-benzotriazole 1-oxide  
4,6-Dichloro-3-methyl-3H-benzotriazole 1-oxide  
5 5,7-Dichloro-6-nitro-3H-benzotriazole 1-oxide  
3,6-Dimethyl-6-nitro-3H-benzotriazole 1-oxide  
3,5-Dimethyl-6-nitro-3H-benzotriazole 1-oxide  
3-Methyl-3H-benzotriazole 1-oxide  
5-Methyl-3H-benzotriazole 1-oxide  
10 6-Methyl-3H-benzotriazole 1-oxide  
6-Methyl-4-nitro-3H-benzotriazole 1-oxide  
7-Methyl-6-nitro-3H-benzotriazole 1-oxide  
5-Chloro-6-nitro-3H-benzotriazole 1-oxide
- 15 **2H-Benzotriazole 1-oxides**  
2-(4-Acetoxy-phenyl)-2H-benzotriazole 1-oxide  
6-Acetylamino-2-phenyl-2H-benzotriazole 1-oxide  
2-(4-Ethyl-phenyl)-4,6-dinitro-2H-benzotriazole 1-oxide  
2-(3-Aminophenyl)-2H-benzotriazole 1-oxide  
20 2-(4-Aminophenyl)-2H-benzotriazole 1-oxide  
6-Amino-2-phenyl-2H-benzotriazole 1-oxide  
5-Bromo-4-chloro-6-nitro-2-phenyl-2H-benzotriazole 1-oxide  
2-(4-Bromophenyl)-2H-benzotriazole 1-oxide  
5-Bromo-2-phenyl-2H-benzotriazole 1-oxide  
25 6-Bromo-2-phenyl-2H-benzotriazole 1-oxide  
2-(4-Bromophenyl)-4,6-dinitro-2H-benzotriazole 1-oxide  
2-(4-Bromophenyl)-6-nitro-2H-benzotriazole 1-oxide  
5-Chloro-2-(2-chlorophenyl)-2H-benzotriazole 1-oxide  
5-Chloro-2-(3-chlorophenyl)-2H-benzotriazole 1-oxide  
30 5-Chloro-2-(2-chlorophenyl)-2H-benzotriazole 1-oxide  
5-Chloro-2-(3-chlorophenyl)-2H-benzotriazole 1-oxide  
5-Chloro-2-(2,4-dibromophenyl)-2H-benzotriazole 1-oxide  
5-Chloro-2-(2,5-dimethylphenyl)-2H-benzotriazole 1-oxide  
5-Chloro-2-(4-nitrophenyl)-2H-benzotriazole 1-oxide

- 5-Chloro-6-nitro-2-phenyl-2H-benzotriazole 1-oxide
- 2-[4-(4-Chloro-3-nitro-phenylazo)-3-nitrophenyl]-4,6-dinitro-2H-benzotriazole 1-oxide
- 2-(3-Chloro-4-nitro-phenyl)-4,6-dinitro-2H-benzotriazole 1-oxide
- 5 2-(4-Chloro-3-nitrophenyl)-4,6-dinitro-2H-benzotriazole 1-oxide
- 4-Chloro-6-nitro-2-p-tolyl-2H-benzotriazole 1-oxide
- 5-Chloro-6-nitro-2-p-tolyl-2H-benzotriazole 1-oxide
- 6-Chloro-4-nitro-2-p-tolyl-2H-benzotriazole 1-oxide
- 2-(2-Chlorophenyl)-2H-benzotriazole 1-oxide
- 10 2-(3-Chlorophenyl)-2H-benzotriazole 1-oxide
- 2-(4-Chlorophenyl)-2H-benzotriazole 1-oxide
- 5-Chloro-2-phenyl-2H-benzotriazole 1-oxide
- 2-[4-(4-Chlorophenylazo)-3-nitrophenyl]-4,6-dinitro-2H-benzotriazole 1-oxide
- 15 2-(2-Chlorophenyl)-4,6-dinitro-2H-benzotriazole 1-oxide
- 2-(3-Chlorophenyl)-4,6-dinitro-2H-benzotriazole 1-oxide
- 2-(4-Chlorophenyl)-4,6-dinitro-2H-benzotriazole 1-oxide
- 2-{4-[N'-(3-Chlorophenyl)-hydrazino]-3-nitrophenyl}4,6-dinitro-2H-benzotriazole 1-oxide
- 20 2-{4-[N'-(4-Chlorophenyl)-hydrazino]-3-nitrophenyl}4,6-dinitro-2H-benzotriazole 1-oxide
- 2-(2-Chlorophenyl)-6-methyl-2H-benzotriazole 1-oxide
- 2-(3-Chlorophenyl)-6-methyl-2H-benzotriazole 1-oxide
- 2-(4-Chlorophenyl)-6-methyl-2H-benzotriazole 1-oxide
- 25 2-(3-Chlorophenyl)-6-nitro-2H-benzotriazole 1-oxide
- 2-(4-Chlorophenyl)-6-nitro-2H-benzotriazole 1-oxide
- 2-(4-Chlorophenyl)-6-picrylazo-2H-benzotriazole 1-oxide
- 5-Chloro-2-(2,4,5-trimethylphenyl)-2H-benzotriazole 1-oxide
- 4,5-Dibromo-6-nitro-2-p-tolyl-2H-benzotriazole 1-oxide
- 30 4,5-Dichloro-6-nitro-2-phenyl-2H-benzotriazole 1-oxide
- 4,5-Dichloro-6-nitro-2-p-tolyl-2H-benzotriazole 1-oxide
- 4,7-Dichloro-6-nitro-2-p-tolyl-2H-benzotriazole 1-oxide
- 4,7-Dimethyl-6-nitro-2-phenyl-2H-benzotriazole 1-oxide
- 2-(2,4-Dimethylphenyl)-4,6-dinitro-benzotriazole 1-oxide

- 2-(2,5-Dimethylphenyl)-4,6-dinitro-2H-benzotriazole 1-oxide  
2-(2,4-Dimethylphenyl)-6-nitro-2H-benzotriazole 1-oxide  
2-(2,5-Dimethylphenyl)-6-nitro-2H-benzotriazole 1-oxide  
4,6-Dinitro-2-[3-nitro-4-(N'-phenylhydrazino)-phenyl-]-2H-benzotriazole  
5 1-oxide  
4,6-Dinitro-2-[4-nitro-4-(N'-phenylhydrazino)-phenyl-]-2H-benzotriazole  
1-oxide  
4,6-Dinitro-2-phenyl-2H-benzotriazole 1-oxide  
2-(2,4-Dinitrophenyl)-4,6-dinitro-2H-benzotriazole 1-oxide  
10 2-(2,4-Dinitrophenyl)-6-nitro-2H-benzotriazole 1-oxide  
4,6-Dinitro-2-o-tolyl-2H-benzotriazole 1-oxide  
4,6-Dinitro-2-p-tolyl-2H-benzotriazole 1-oxide  
4,6-Dinitro-2-(2,4,5-trimethylphenyl)-2H-benzotriazole 1-oxide  
2-(4-Methoxyphenyl)-2H-benzotriazole 1-oxide  
15 2-(4-Methoxyphenyl)-6-methyl-2H-benzotriazole 1-oxide  
5-Methyl-6-nitro-2-m-tolyl-2H-benzotriazole 1-oxide  
5-Methyl-6-nitro-2-o-tolyl-2H-benzotriazole 1-oxide  
5-Methyl-6-nitro-2-p-tolyl-2H-benzotriazole 1-oxide  
6-Methyl-4-nitro-2-p-tolyl-2H-benzotriazole 1-oxide  
20 6-Methyl-2-phenyl-2H-benzotriazole 1-oxide  
4-Methyl-2-m-tolyl-2H-benzotriazole 1-oxide  
4-Methyl-2-o-tolyl-2H-benzotriazole 1-oxide  
4-Methyl-2-p-tolyl-2H-benzotriazole 1-oxide  
6-Methyl-2-m-tolyl-2H-benzotriazole 1-oxide  
25 6-Methyl-2-o-tolyl-2H-benzotriazole 1-oxide  
6-Methyl-2-p-tolyl-2H-benzotriazole 1-oxide  
2-[1]Naphthyl-4,6-dinitro-2H-benzotriazole 1-oxide  
2-[2]Naphthyl-4,6-dinitro-2H-benzotriazole 1-oxide  
2-[1]Naphthyl-6-nitro-2H-benzotriazole 1-oxide  
30 2-[2]Naphthyl-6-nitro-2H-benzotriazole 1-oxide  
2-(3-Nitrophenyl)-2H-benzotriazole 1-oxide  
6-Nitro-2-phenyl-2H-benzotriazole 1-oxide  
4-Nitro-2-p-tolyl-2H-benzotriazole 1-oxide  
6-Nitro-2-o-tolyl-2H-benzotriazole 1-oxide

6-Nitro-2-p-tolyl-2H-benzotriazole 1-oxide

6-Nitro-2-(2,4,5-trimethylphenyl)-2H-benzotriazole 1-oxide

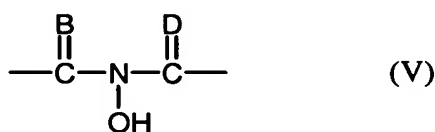
2-Phenyl-2H-benzotriazole 1-oxide

2-o-Tolyl-2H-benzotriazole 1-oxide

5 2-p-Tolyl-2H-benzotriazole 1-oxide

The mediator may preferably be further selected from the group of cyclic N-hydroxy compounds having at least one optionally substituted five- or six-membered ring containing the structure identified in the general formula (V)

10

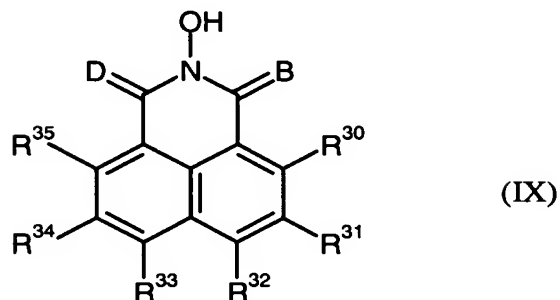
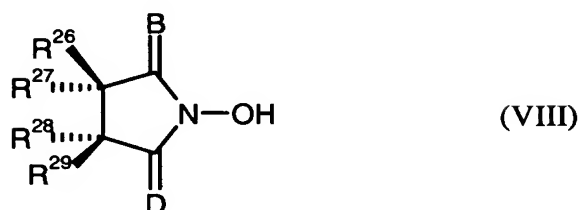
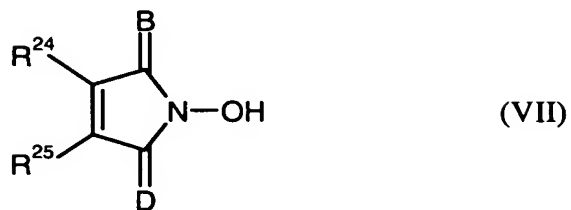
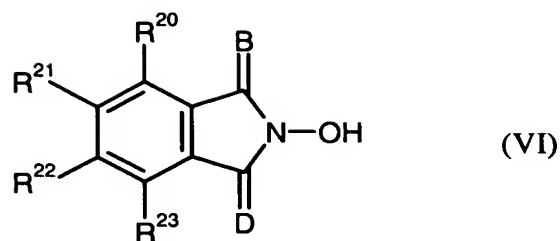


and also salts, ethers or esters thereof, where

15 B and D are the same or different and denote oxygen, sulfur or  $\text{NR}^{18}$ , where

$\text{R}^{18}$  represents hydrogen, hydroxyl, formyl, carbamoyl, sulfo, esters or salts thereof, sulfamoyl, nitro, amino, phenyl, aryl- $\text{C}_1\text{-C}_5\text{-alkyl}$ ,  $\text{C}_1\text{-C}_{12}\text{-alkyl}$ ,  $\text{C}_1\text{-C}_5\text{-alkoxy}$ ,  $\text{C}_1\text{-C}_{10}\text{-carbonyl}$ , carbonyl- $\text{C}_1\text{-C}_6\text{-alkyl}$ , phospho, phosphono or phosphonooxy and  
 20 also esters or salts thereof, where the carbamoyl, sulfamoyl, amino and phenyl radicals may be unsubstituted or singly or multiply  $\text{R}^{19}$  substituted and the aryl- $\text{C}_1\text{-C}_5\text{-alkyl}$ ,  $\text{C}_1\text{-C}_{12}\text{-alkyl}$ ,  $\text{C}_1\text{-C}_5\text{-alkoxy}$ ,  $\text{C}_1\text{-C}_{10}\text{-carbonyl}$  and carbonyl- $\text{C}_1\text{-C}_6\text{-alkyl}$  radicals may be saturated or unsaturated, branched or unbranched and may similarly be singly or multiply  $\text{R}^{19}$  substituted, where  $\text{R}^{19}$  in  
 25 each occurrence is the same or different and denotes hydroxyl, formyl or carboxyl and also esters or salts thereof, carbamoyl or sulfo, esters or salts thereof, sulfamoyl, nitro, amino, phenyl,  $\text{C}_1\text{-C}_5\text{-alkyl}$  or  $\text{C}_1\text{-C}_5\text{-alkoxy}$ .

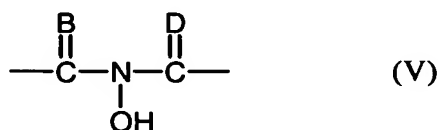
Preferably the mediator is selected from the group of compounds of the general  
 30 formula (VI), (VII), (VIII) or (IX)



5

where B and D are each as defined above and the radicals  $R^{20}$ - $R^{35}$  are the same or different and have halogen, carboxyl, salts or esters of carboxyl or have the meanings defined for  $R^{18}$ , although  $R^{26}$  and  $R^{27}$  on the one hand and  $R^{28}$  and  $R^{29}$  on the other must not both denote hydroxyl or amino and optionally any two of the substituents  $R^{20}$ - $R^{23}$ ,  $R^{24}$ - $R^{25}$ ,  $R^{26}$ - $R^{29}$ ,  $R^{30}$ - $R^{35}$  may be linked together to form a ring -E-, where -E- has one of the following meanings:

(-CH=CH)<sub>n</sub> with n = 1 to 3, -CH=CH-CH=N- or



15

and where optionally the radicals  $R^{26}$ - $R^{29}$  may also be bonded together by one or two bridge elements -F-, where -F- in each occurrence is the same or different and has one of the following meanings: -O-, -S-, -CH<sub>2</sub>-, -CR<sup>36</sup>=CR<sup>37</sup>-, where  $R^{36}$  and  $R^{37}$  are the same or different and have the meaning of  $R^{20}$ .

5

Compounds which are particularly preferred for use as mediators have the general formulae (VI), (VII), (VIII) or (IX) wherein B and D denote oxygen or sulfur.

10 Examples of such compounds are N-hydroxyphthalimide and also optionally substituted N-hydroxyphthalimide derivatives, N-hydroxymaleimide and also optionally substituted N-hydroxymaleimide derivatives, N-hydroxynaphthalimide and also optionally substituted N-hydroxynaphthaleneimide derivatives, N-hydroxysuccinimide and optionally substituted N-hydroxysuccinimide derivatives, preferably those wherein the radicals  $R^{26}$ - $R^{29}$  are bonded together to form polycyclic  
15 structures.

Examples of compounds of the formula (VI) useful as a mediator are:

20 N-Hydroxyphthalimide  
4-Amino-N-hydroxyphthalimide  
3-Amino-N-hydroxyphthalimide  
N-Hydroxy-benzene-1,2,4-tricarboximide  
N,N'-Dihydroxy-pyromellitic diimide  
N,N'-Dihydroxy-benzophenone-3,3',4,4'-tetracarboxylic diimide.

25

Examples of compounds of the formula (VII) useful as a mediator are:

N-Hydroxymaleimide  
Pyridine-2,3-dicarboxylic N-hydroxyimide.

30

Examples of compounds of the formula (VIII) useful as a mediator are:

N-Hydroxysuccinimide  
N-Hydroxytartarimide

N-Hydroxy-5-norbornene-2,3-dicarboxylic imide

exo-N-Hydroxy-7-oxabicyclo[2.2.1]-hept-5-ene-2,3-dicarboximide

N-Hydroxy-cis-cyclohexane-1,2-dicarboximide

N-Hydroxy-cis-4-cyclohexene-1,2-dicarboximide.

5

An example of a compound of the formula (IX) useful as a mediator is:

N-Hydroxynaphthalimide sodium salt

- 10 An example of a useful mediator having a six-membered ring containing the structure identified in the formula (V) is:

N-Hydroxyglutarimide

- 15 The compounds identified by way of example are also useful as a mediator in the form of their salts or esters.

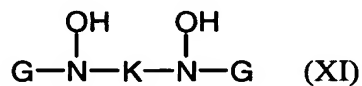
Compounds likewise useful as a mediator are selected from the group of **N-aryl-N-hydroxyamides**.

20

Of these it is preferably the compounds of the general formula (X), (XI) or (XII) which are used as mediators



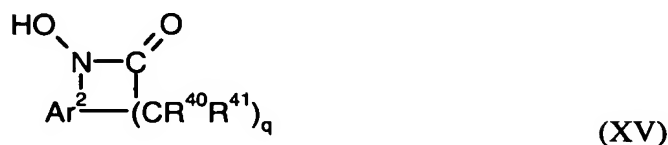
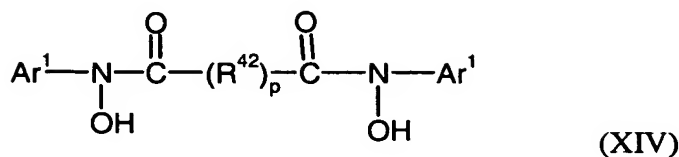
25



- 30 and also salts, ethers or esters thereof, where

G is a monovalent homo- or heteroaromatic mono- or binuclear radical and

- L is a bivalent homo- or heteroaromatic mono- or binuclear radical and where these aromatic radicals may be substituted by one or more, identical or different  $R^{38}$  radicals, where  $R^{38}$  may represent halogen, hydroxyl, formyl, cyano, carbamoyl, carboxyl, esters or salts thereof, sulfo, esters or salts thereof, sulfamoyl, nitro, nitroso, amino, phenyl, aryl- $C_1$ - $C_5$ -alkyl,  $C_1$ - $C_{12}$ -alkyl,  $C_1$ - $C_5$ -alkoxy,  $C_1$ - $C_{10}$ -carbonyl, carbonyl- $C_1$ - $C_6$ -alkyl, phospho, phosphono, phosphonooxy, esters or salts thereof, where the carbamoyl, sulfamoyl, amino and phenyl radicals may in turn be unsubstituted or singly or multiply  $R^{39}$  substituted and the aryl- $C_1$ - $C_5$ -alkyl  $C_1$ - $C_{12}$ -alkyl,  $C_1$ - $C_5$ -alkoxy,  $C_1$ - $C_{10}$ -carbonyl, carbonyl- $C_1$ - $C_6$ -alkyl radicals may be saturated or unsaturated, branched or unbranched and may similarly be singly or multiply  $R^{39}$  substituted, where  $R^{39}$  in each occurrence is the same or different and denotes hydroxyl, formyl, cyano, carboxyl, esters or salts thereof, carbamoyl, sulfo, sulfamoyl, nitro, nitroso, amino, phenyl,  $C_1$ - $C_5$ -alkyl,  $C_1$ - $C_5$ -alkoxy,  $C_1$ - $C_5$ -alkylcarbonyl and two  $R^{38}$  or  $R^{39}$  radicals at a time may be linked together pairwise via a  $[-CR^{40}R^{41}-]_m$  bridge, where m is 0,1,2, 3 or 4, and  $R^{40}$  and  $R^{41}$  are the same or different and denote carboxyl, esters or salts thereof, phenyl,  $C_1$ - $C_5$ -alkyl,  $C_1$ - $C_5$ -alkoxy or  $C_1$ - $C_5$ -alkylcarbonyl and one or more nonadjacent  $[-CR^{40}R^{41}-]$  groups may be replaced by O, S or an optionally  $C_1$ - $C_5$ -alkyl-substituted imino radical and two adjacent  $[-CR^{40}R^{41}-]$  groups by a  $[-CR^{40}=CR^{41}]$  group and denotes a monovalent acid radical present in amidic form of acids selected from the group consisting of carboxylic acids having up to 20 carbon atoms, carbonic acid, half esters of carbonic acid or of carbamic acid, sulfonic acid, phosphonic acid, phosphoric acid, monoesters of phosphoric acid, and diesters of phosphoric acid and K is a divalent acid radical present in amidic form of acids selected from the group consisting of mono- and dicarboxylic acids having up to 20 carbon atoms, carbonic acid, sulfonic acid, phosphonic acid, phosphoric acid, monoesters of phosphoric acid.
- Particularly preferred mediators include compounds of the general formula (XIII), (XIV), (XV), (XVI) or (XVII)



5

and also salts, ethers or esters thereof, where

$\text{Ar}^1$  denotes a univalent homo- or heteroaromatic mononuclear aryl radical and

10

$\text{Ar}^2$  denotes a bivalent homo- or heteroaromatic mononuclear aryl radical which may each be substituted by one or more, identical or different  $\text{R}^{44}$  radicals, where  $\text{R}^{44}$  represents hydroxyl, cyano, carboxyl, esters or salts thereof, sulfo, esters or salt thereof, nitro, nitroso, amino,  $\text{C}_1$ - $\text{C}_{12}$ -alkyl,  $\text{C}_1$ - $\text{C}_5$ -alkoxy,  $\text{C}_1$ - $\text{C}_{10}$ -carbonyl, carbonyl or  $\text{C}_1$ - $\text{C}_6$ -alkyl, where the amino radicals may be unsubstituted or singly or multiply  $\text{R}^{45}$  substituted and the  $\text{C}_1$ - $\text{C}_5$ -alkyl,  $\text{C}_1$ - $\text{C}_5$ -alkoxy,  $\text{C}_1$ - $\text{C}_{10}$ -carbonyl and carbonyl- $\text{C}_1$ - $\text{C}_6$ -alkyl radicals may be saturated or unsaturated, branched or unbranched and may similarly be singly or multiply  $\text{R}^{45}$  substituted, where  $\text{R}^{45}$  in each occurrence is the same or different and denotes hydroxyl, carboxyl, esters or salts thereof, sulfo, nitro, amino,  $\text{C}_1$ - $\text{C}_5$ -alkyl,  $\text{C}_1$ - $\text{C}_5$ -alkoxy or  $\text{C}_1$ - $\text{C}_5$ -alkylcarbonyl and two  $\text{R}^{44}$  radicals at a time may be linked together pairwise via a  $[-\text{CR}^{40}\text{R}^{41}-]_m$  bridge where m is 0, 1, 2, 3 or 4, and

20

$R^{40}$  and  $R^{41}$  are each as defined above and one or more nonadjacent  $[-CR^{40}R^{41}-]$  groups may be replaced by O, S or an optionally  $C_1-C_5$ -alkyl-substituted imino radical and two adjacent  $[-CR^{40}R^{41}-]$  groups may be replaced by a  $[-CR^{40}=CR^{41}-]$  group,

5

$R^{42}$  in each occurrence is the same or different and denotes hydrogen, phenyl, aryl- $C_1-C_5$ -alkyl,  $C_1-C_{12}$ -alkyl,  $C_1-C_5$ -alkoxy or  $C_1-C_{10}$ -carbonyl, where the phenyl radicals may be unsubstituted or singly or multiply  $R^{46}$  substituted and the aryl- $C_1-C_5$ -alkyl,  $C_1-C_{12}$ -alkyl,  $C_1-C_5$ -alkoxy,  $C_1-C_5$ -carbonyl radicals may be saturated or unsaturated, branched or unbranched and may similarly be singly or multiply  $R^{46}$  substituted, where

10

$R^{46}$  in each occurrence is the same or different and denotes hydroxyl, formyl, cyano, carboxyl, esters or salts thereof, carbamoyl, sulfo, sulfamoyl, nitro, nitroso, amino, phenyl,  $C_1-C_5$ -alkyl or  $C_1-C_5$ -alkoxy and  $R^{43}$  denotes divalent radicals ortho-, meta-, para-phenylene, aryl- $C_1-C_6$ -alkyl,  $C_1-C_{12}$ -alkylene or  $C_1-C_5$ -alkylenedioxy, where the phenylene radicals may be unsubstituted or singly or multiply  $R^{46}$  substituted and the aryl- $C_1-C_5$ -alkyl,  $C_1-C_{12}$ -alkyl and  $C_1-C_5$ -alkoxy radicals may be saturated or unsaturated, branched or unbranched and may be singly or multiply  $R^{46}$  substituted, where

15

20

p denotes 0 or 1 and

q denotes an integer from 1 to 3.

25

Preferably, Ar denotes a phenyl radical and  $Ar^2$  denotes an ortho-phenylene radical, where  $Ar^1$  may be substituted by up to five and,  $Ar^2$  by up to four, identical or different radicals  $C_1-C_3$ -alkyl,  $C_1-C_3$ -alkylcarbonyl, carboxyl, esters or salts thereof, sulfo, esters or salts thereof, hydroxyl, cyano, nitro, nitroso or amino, where amino radicals may be substituted with two different radicals selected from the group consisting of hydroxyl and  $C_1-C_3$ -alkylcarbonyl.

30

Preferably  $R^{42}$  represents a univalent radical selected from the group consisting of hydrogen, phenyl,  $C_1-C_{12}$ -alkyl and  $C_1-C_5$ -alkoxy, where the  $C_1-C_{12}$ -alkyl and  $C_1-C_5$ -

alkoxy may be saturated or unsaturated, branched or unbranched.

Preferably  $R^{43}$  represents a bivalent radical: ortho- or para-phenylene,  $C_1$ - $C_{12}$ -alkylene or  $C_1$ - $C_5$ -alkylenedioxy, where the aryl- $C_1$ - $C_5$ -alkyl,  $C_1$ - $C_{12}$ -alkyl and  
 5  $C_1$ - $C_5$ -alkoxy radicals may be saturated or unsaturated, branched or unbranched and may be singly or multiply  $R^{46}$  substituted.

Preferably  $R^{46}$  denotes a carboxyl radical, esters or salts thereof, a carbamoyl, phenyl or  $C_1$ - $C_3$ -alkoxy radical.

10

Examples of compounds useful as mediators are:

N-Hydroxyacetanilide,  
 N-Hydroxypivaloylanilide,  
 15 N-Hydroxyacryloylanilide,  
 N-Hydroxybenzoylanilide,  
 N-Hydroxy-methylsulfonylanilide,  
 Methyl N-hydroxy-N-phenylcarbamate,  
 N-Hydroxy-3-oxobutyrylanilide,  
 20 N-Hydroxy-4-cyanoacetanilide, N-hydroxy-4-methoxyacetanilide,  
 N-Hydroxyphenacetin,  
 N-Hydroxy-2,3-dimethylacetanilide,  
 N-Hydroxy-2-methylacetanilide,  
 N-Hydroxy-4-methylacetanilide,  
 25 1-Hydroxy-3,4-dihydroquinolin-(1H)-2-one,  
 N,N'-Dihydroxy-N,N'-diacetyl-1,3-phenylenediamine,  
 N,N'-Dihydroxy-succinic dianilide,  
 N,N'-Dihydroxy-maleic dianilide,  
 N,N'-Dihydroxy-oxalic dianilide,  
 30 N,N'-Dihydroxy-phosphoric dianilide,  
 N-Acetoxyacetanilide,  
 N-Hydroxymethyloxalyanilide,  
 N-Hydroxymaleic monoanilide.

Preferred for use as mediators are

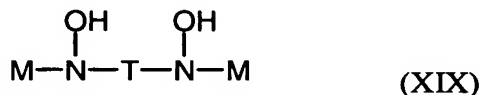
- N-Hydroxyacetanilide,  
 N-Hydroxyformanilide,  
 5 Methyl N-hydroxy-N-phenylcarbamate,  
 N-Hydroxy-2-methylacetanilide,  
 N-Hydroxy-4-methylacetanilide,  
 1-Hydroxy-3,4-dihydroquinolin-(1H)-2-one and also  
 N-Acetoxyacetanilide.

10

The mediator may further be selected from the group of **N-alkyl-N-hydroxyamides**.

Preference for use as mediators in this context is given to compounds of the general formula (XVIII) or (XIX)

15



and also salts, ethers or esters thereof, where

20

- M in each occurrence is the same or different and denotes a univalent linear or branched, cyclic or polycyclic, saturated or unsaturated C<sub>1</sub>-C<sub>24</sub>-alkyl radical and where this alkyl radical may be substituted by one or more R<sup>48</sup> radicals, where R<sup>48</sup> in each occurrence is the same or different and denotes hydroxyl, mercapto, formyl, carbamoyl, carboxyl, esters or salts thereof, sulfo, esters or salts thereof, sulfamoyl, nitro, nitroso, amino, hydroxylamino, phenyl, C<sub>1</sub>-C<sub>5</sub>-alkoxy, C<sub>1</sub>-C<sub>10</sub>-carbonyl, phospho, phosphono or phosphonooxy and also esters or salts thereof and where the carbamoyl, sulfamoyl, amino, hydroxylamino, mercapto and phenyl radicals may be unsubstituted or singly or multiply R<sup>48</sup> substituted and the C<sub>1</sub>-C<sub>5</sub>-alkoxy and C<sub>1</sub>-C<sub>10</sub>-carbonyl radicals may be saturated or unsaturated, branched or unbranched and may be singly or multiply R<sup>48</sup> substituted, where R<sup>48</sup> in each occurrence is the same or different and denotes hydroxyl, formyl, cyano, carboxyl, esters or salts
- 25
- 30

thereof, carbamoyl, sulfo, sulfamoyl, nitro, nitroso, amino, phenyl, benzoyl, C<sub>1</sub>-C<sub>5</sub>-alkyl, C<sub>1</sub>-C<sub>5</sub>-alkoxy or C<sub>1</sub>-C<sub>5</sub>-alkylcarbonyl and non- $\alpha$ -disposed methylene groups may be replaced by oxygen or sulfur or an optionally monosubstituted imino radical, and

5

N''' denotes a monovalent acid radical in amidic form of acids which are aliphatic, mono- or binuclear aromatic or mono- or binuclear heteroaromatic carboxylic acids having 1-20 carbon atoms, carbonic acid, half esters of carbonic acid or of carbamic acid, sulfonic acid, phosphonic acid, phosphoric acid, monoesters of phosphoric acid or diesters of phosphoric acid, and

10

T denotes a bivalent acid radical in amidic form of acids which are aliphatic, mono- or binuclear aromatic or mono- or binuclear heteroaromatic dicarboxylic acids having 1-20 carbon atoms, carbonic acid, sulfonic acid, phosphonic acid, phosphoric acid or monoesters of phosphoric acid, and where alkyl radicals of the aliphatic acids N''' and T which are present in amidic form may be linear or branched, cyclic and/or polycyclic, saturated or unsaturated and contain 1-24 carbon atoms and are unsubstituted or singly or multiply R<sup>47</sup> substituted and where, furthermore, aryl and heteroaryl radicals of the aromatic or heteroaromatic acids N''' and T which are present in amidic form may be substituted by one or more R<sup>49</sup> radicals, where R<sup>49</sup> in each occurrence is the same or different and denotes hydroxyl, mercapto, formyl, cyano, carbamoyl, carboxyl, esters or salts thereof, sulfo, esters or salts thereof, sulfamoyl, nitro, nitroso, amino, phenyl, aryl-C<sub>1</sub>-C<sub>5</sub>-alkyl, C<sub>1</sub>-C<sub>12</sub>-alkyl, C<sub>1</sub>-C<sub>5</sub>-alkoxy, C<sub>1</sub>-C<sub>10</sub>-carbonyl, phospho, phosphono or phosphonooxy and also esters or salts thereof and where carbamoyl, sulfamoyl, amino, mercapto and phenyl radicals may be unsubstituted or singly or multiply R<sup>48</sup> substituted and the aryl-C<sub>1</sub>-C<sub>5</sub>-alkyl, C<sub>1</sub>-C<sub>12</sub>-alkyl-C<sub>1</sub>-C<sub>5</sub>-alkoxy, C<sub>1</sub>-C<sub>10</sub>-carbonyl radicals may be saturated or unsaturated, branched or unbranched and may be singly or multiply R<sup>48</sup> substituted.

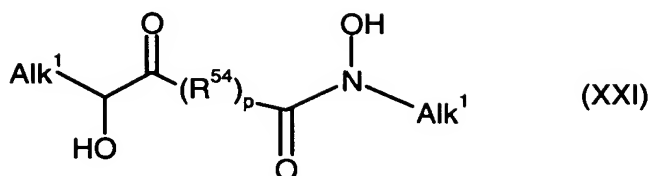
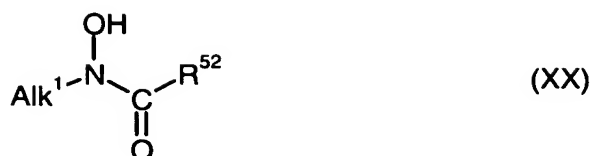
15

20

25

30

Particular preference for use as mediators is given to compounds having the general formulae (XX), (XXI), (XXII) or (XXIII):



5

and also salts, ethers or esters thereof, where

Alk<sup>1</sup> in each occurrence is the same or different and denotes a univalent linear or branched, cyclic or polycyclic, saturated or unsaturated C<sub>1</sub>-C<sub>10</sub>-alkyl radical,

10

where this alkyl radical may be substituted by one or more R<sup>50</sup> radicals, where R<sup>50</sup> in each occurrence is the same or different and denotes hydroxyl, formyl, carbamoyl, carboxyl, esters or salts thereof, sulfo, esters or salts thereof, sulfamoyl, nitro, nitroso, amino, hydroxylamino, phenyl, C<sub>1</sub>-C<sub>5</sub>-alkoxy or C<sub>1</sub>-C<sub>5</sub>-carbonyl and where the carbamoyl, sulfamoyl, amino, hydroxylamino and phenyl radicals may be unsubstituted or singly or multiply R<sup>51</sup> substituted and the C<sub>1</sub>-C<sub>5</sub>-alkoxy and C<sub>1</sub>-C<sub>10</sub>-carbonyl radicals may be saturated or unsaturated, branched or unbranched and may be singly or multiply R<sup>51</sup> substituted, where

15

20

R<sup>51</sup> in each occurrence is the same or different and denotes hydroxyl, formyl, cyano, carboxyl, esters or salts thereof, carbamoyl, sulfo, sulfamoyl, nitro, amino, phenyl, benzoyl, C<sub>1</sub>-C<sub>5</sub>-alkyl, C<sub>1</sub>-C<sub>5</sub>-alkoxy or C<sub>1</sub>-C<sub>5</sub>-alkylcarbonyl and non-α-disposed methylene groups may be replaced by oxygen or sulfur or an optionally monosubstituted imino radical, and where

$R^{52}$  denotes identical or different univalent radicals hydrogen, phenyl, pyridyl, furyl, pyrrolyl, thienyl, aryl  $C_1$ - $C_5$ -alkyl,  $C_1$ - $C_{12}$ -alkyl,  $C_1$ - $C_{10}$ -alkoxy or  $C_1$ - $C_{10}$ -carbonyl, where the phenyl, pyridyl, furyl, pyrrolyl and thienyl radicals may be unsubstituted or singly or multiply  $R^{53}$  substituted and the aryl- $C_1$ - $C_5$ -alkyl,  $C_1$ - $C_{12}$ -alkyl,  $C_1$ - $C_5$ -alkoxy and  $C_1$ - $C_{10}$ -carbonyl radicals may be saturated or unsaturated, branched or unbranched and may similarly be singly or multiply  $R^{53}$  substituted, where

$R^{53}$  in each occurrence is the same or different and denotes hydroxyl, formyl, carboxyl, esters or salts thereof, carbamoyl, sulfo, sulfamoyl, nitro, amino, phenyl,  $C_1$ - $C_5$ -alkyl or  $C_1$ - $C_5$ -alkoxy, and

$R^{54}$  denotes bivalent radicals phenylene, pyridylene, thienylene, furylene, pyrrolylene, aryl- $C_1$ - $C_5$ -alkyl,  $C_1$ - $C_{12}$ -alkylene,  $C_1$ - $C_5$ -alkylenedioxy, where phenylene, pyridylene, thienylene, furylene or pyrrolylene may be unsubstituted or singly or multiply  $R^{53}$  substituted and the aryl- $C_1$ - $C_5$ -alkyl,  $C_1$ - $C_{12}$ -alkyl,  $C_1$ - $C_5$ -alkoxy radicals may be saturated or unsaturated, branched or unbranched and may similarly be singly or multiply  $R^{53}$  substituted, where p denotes 0 or 1.

Very particular preference for use as mediators is given to compounds having the general formula (XX), (XXI), (XXII) and (XXIII) wherein

$Alk^1$  in each occurrence is the same or different and denotes a univalent, linear, branched or cyclic, saturated or unsaturated  $C_1$ - $C_{10}$ -alkyl radical, where this alkyl radical may be substituted by one or more  $R^{50}$  radicals, where  $R^{50}$  in each occurrence is the same or different and denotes hydroxyl, carbamoyl, carboxyl, esters or salts thereof, sulfo, esters or salts thereof, sulfamoyl, amino, phenyl,  $C_1$ - $C_5$ -alkoxy or  $C_1$ - $C_5$ -carbonyl and where the carbamoyl, sulfamoyl, amino and phenyl radicals may be unsubstituted or singly or multiply  $R^{51}$  substituted and the  $C_1$ - $C_5$ -alkoxy and  $C_1$ - $C_{10}$ -carbonyl radicals may be saturated or unsaturated, branched or unbranched and may similarly be singly or multiply  $R^{51}$  substituted, where  $R^{51}$  in each occurrence is the same or different and denotes hydroxyl, carboxyl, esters or salts thereof, carbamoyl, sulfo, sulfamoyl, nitro, amino, phenyl, benzoyl,  $C_1$ - $C_5$ -alkyl,  $C_1$ - $C_5$ -alkoxy or  $C_1$ - $C_5$ -alkylcarbonyl and

where  $R^{52}$  denotes identical or different univalent radicals hydrogen, phenyl, furyl, aryl- $C_1-C_5$ -alkyl,  $C_1-C_{12}$ -alkyl,  $C_1-C_{10}$ -alkoxy or  $C_1-C_{10}$ -carbonyl, where the phenyl and furyl radicals may be unsubstituted or singly or multiply  $R^{53}$  substituted and the  
 5 saturated or unsaturated, branched or unbranched and may be singly or multiply  $R^{53}$  substituted, where

$R^{53}$  in each occurrence is the same or different and denotes carboxyl, esters or salts thereof, carbamoyl, phenyl,  $C_1-C_5$ -alkyl or  $C_1-C_5$ -alkoxy, and

10

$R^{54}$  denotes a bivalent radical phenylene, furylene,  $C_1-C_{12}$ -alkylene and  $C_1-C_5$ -alkylenedioxy, where phenylene and furylene may be unsubstituted or singly or multiply  $R^{53}$  substituted and the aryl- $C_1-C_5$ -alkyl,  $C_1-C_{12}$ -alkyl,  $C_1-C_5$ -alkoxy radicals may be saturated or unsaturated, branched or unbranched and may be singly  
 15 or multiply  $R^{53}$  substituted,

where p denotes 0 or 1.

Examples of compounds useful as mediators are

20

N-Hydroxy-N-methyl-benzamide,  
 N-Hydroxy-N-methyl-benzenesulfonamide,  
 N-Hydroxy-N-methyl-p-toluenesulfonamide,  
 N-Hydroxy-N-methyl-furan-2-carboxamide,  
 25 N-Hydroxy-N-methyl-thiophene-2-carboxamide,  
 N,N'-Dihydroxy-N,N'-dimethyl-phthalamide,  
 N,N'-Dihydroxy-N,N'-dimethyl-isophthalamide,  
 N,N'-Dihydroxy-N,N'-dimethyl-terephthalamide,  
 N,N'-Dihydroxy-N,N'-dimethyl-benzene-1,3-disulfonamide,  
 30 N,N'-Dihydroxy-N,N'-dimethyl-furan-3,4-dicarboxamide,  
 N-Hydroxy-N-tert-butyl-benzamide,  
 N-Hydroxy-N-tert-butyl-benzenesulfonamide,  
 N-Hydroxy-N-tert-butyl-p-toluenesulfonamide,  
 N-Hydroxy-N-tert-butyl-furan-2-carboxamide,

- N-Hydroxy-N-tert-butyl-thiophene-2-carboxamide,  
N,N'-Dihydroxy-N,N'-di-tert-butyl-phthalamide,  
N,N'-Dihydroxy-N,N'-di-tert-butyl-isophthalamide,  
N,N'-Dihydroxy-N,N'-di-tert-butylterephthalamide,  
5 N,N'-Dihydroxy-N,N'-di-tert-butyl-benzene-1,3-disulfonamide,  
N,N'-Dihydroxy-N,N'-di-tert-butyl-furan-3,4-dicarboxamide,  
N-Hydroxy-N-cyclohexyl-benzamide,  
N-Hydroxy-N-cyclohexylbenzenesulfonamide,  
N-Hydroxy-N-cyclohexyl-p-toluenesulfonamide,  
10 N-Hydroxy-N-cyclohexyl-furan-2-carboxamide,  
N-Hydroxy-N-cyclohexyl-thiophene-2-carboxamide,  
N,N'-Dihydroxy-N,N'-dicyclohexyl-phthalamide,  
N,N'-Dihydroxy-N,N'-dicyclohexyl-isophthalamide,  
N,N'-Dihydroxy-N,N'-dicyclohexyl-terephthalamide,  
15 N,N'-Dihydroxy-N,N'-dicyclohexyl-benzene-1,3-disulfonamide,  
N,N'-Dihydroxy-N,N'-dicyclohexyl-furan-3,4-dicarboxamide,  
N-Hydroxy-N-isopropyl-benzamide,  
N-Hydroxy-N-isopropylbenzene-sulfonamide,  
N-Hydroxy-N-isopropyl-p-toluenesulfonamide,  
20 N-Hydroxy-N-isopropyl-furan-2-carboxamide,  
N-Hydroxy-N-isopropyl-thiophene-2-carboxamide,  
N,N'-Dihydroxy-N,N'-diisopropyl-phthalamide,  
N,N'-Dihydroxy-N,N'-diisopropyl-isophthalamide,  
N,N'-Dihydroxy-N,N'-diisopropyl-terephthalamide,  
25 N,N'-Dihydroxy-N,N'-diisopropyl-benzene-1,3-disulfonamide,  
N,N'-Dihydroxy-N,N'-diisopropyl-furan-3,4-dicarboxamide,  
N-Hydroxy-N-methyl-acetamide,  
N-Hydroxy-N-tert-butyl-acetamide,  
N-Hydroxy-N-isopropyl-acetamide,  
30 N-Hydroxy-N-cyclohexyl-acetamide,  
N-Hydroxy-N-methyl-pivalamide,  
N-Hydroxy-N-isopropyl-pivalamide,  
N-Hydroxy-N-methyl-acrylamide,  
N-Hydroxy-N-tert-butyl-acrylamide,

- 5 N-Hydroxy-N-isopropyl-acrylamide,  
N-Hydroxy-N-cyclohexyl-acrylamide,  
N-Hydroxy-N-methyl-methanesulfonamide,  
N-Hydroxy-N-isopropylmethanesulfonamide,  
Methyl N-hydroxy-N-isopropylcarbamate,  
N-Hydroxy-N-methyl-3-oxo-butyramide,  
N,N'-Dihydroxy-N,N'-dibenzoyl-ethylenediamine,  
N,N'-Dihydroxy-N,N'-dimethylsuccinamide,  
N,N'-Dihydroxy-N,N'-di-tert-butyl-maleimide,  
10 N-Hydroxy-N-tert-butyl-maleic monoamide,  
N,N'-Dihydroxy-N,N'-di-tert-butyl-oxalamide,  
N,N'-Dihydroxy-N,N'-di-tert-butyl-phosphoramidate.

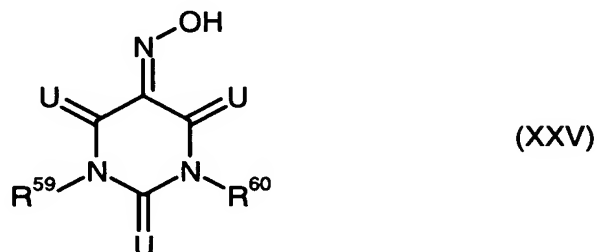
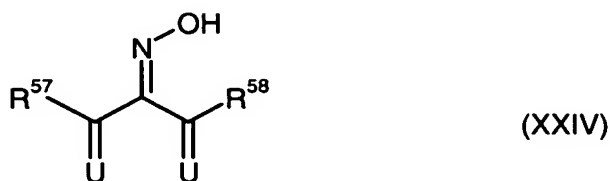
- 15 Preference for use as mediators is given to compounds selected from the group consisting of

- 20 N-Hydroxy-N-methyl-benzamide,  
N-Hydroxy-N-methylbenzenesulfonamide,  
N-Hydroxy-N-methyl-p-toluenesulfonamide,  
N-Hydroxy-N-methylfuran-2-carboxamide,  
N,N'-Dihydroxy-N,N'-dimethyl-phthalamide,  
N,N'-Dihydroxy-N,N'-dimethyl-terephthalamide,  
N,N'-Dihydroxy-N,N'-dimethyl-benzene-1,3-disulfonamide,  
N-Hydroxy-N-tert-butyl-benzamide,  
25 N-Hydroxy-N-tert-butyl-benzenesulfonamide,  
N-Hydroxy-N-tert-butyl-p-toluenesulfonamide,  
N-Hydroxy-N-tert-butyl-furan-2-carboxamide,  
N,N'-Dihydroxy-N,N'-di-tert-butyl-terephthalamide,  
N-Hydroxy-N-isopropyl-benzamide,  
30 N-Hydroxy-N-isopropyl-p-toluenesulfonamide,  
N-Hydroxy-N-isopropyl-furan-2-carboxamide,  
N,N'-Dihydroxy-N,N'-diisopropyl-terephthalamide,  
N,N'-Dihydroxy-N,N'-diisopropyl-benzene-1,3-disulfonamide,  
N-Hydroxy-N-methyl-acetamide,

- N-Hydroxy-N-tert-butyl-acetamide,  
 N-Hydroxy-N-isopropylacetamide,  
 N-Hydroxy-N-cyclohexyl-acetamide,  
 N-Hydroxy-N-methyl-pivalamide,  
 5 N-Hydroxy-N-tert-butyl-acrylamide,  
 N-Hydroxy-N-isopropyl-acrylamide,  
 N-Hydroxy-N-methyl-3-oxo-butyramide,  
 N,N'-Dihydroxy-N,N'-dibenzoyl-ethylenediamine,  
 N,N'-Dihydroxy-N,N'-di-tert-butyl-maleiimide,  
 10 N-Hydroxy-N-tert-butyl-maleic monoamide,  
 N,N'-Dihydroxy-N,N'-di-tert-butyl-oxalamide.

The mediator may further be selected from the group of **oximes** of the general formula (XXIV) or (XXV)

15



and also salts, ethers or esters thereof, where

- 20 U in each occurrence is the same or different and denotes oxygen, sulfur or  $\text{NR}^{55}$ , where

- $\text{R}^{55}$  denotes hydrogen, hydroxyl, formyl, carbamoyl, sulfo, esters or salts thereof,  
 sulfamoyl, nitro, amino, phenyl, aryl- $\text{C}_1$ - $\text{C}_5$ -alkyl,  $\text{C}_1$ - $\text{C}_{12}$ -alkyl,  $\text{C}_1$ - $\text{C}_5$ -alkoxy,  
 25  $\text{C}_1$ - $\text{C}_{10}$ -carbonyl, carbonyl- $\text{C}_1$ - $\text{C}_6$ -alkyl, phospho, phosphono or phosphonooxy and  
 also esters or salts thereof,

where the carbamoyl, sulfamoyl, amino and phenyl radicals may be unsubstituted or singly or multiply  $R^{56}$  substituted and the aryl- $C_1$ - $C_5$ -alkyl,  $C_1$ - $C_{10}$ -alkyl,  $C_1$ - $C_5$ -alkoxy,  $C_1$ - $C_{10}$ -carbonyl and carbonyl- $C_1$ - $C_6$ -alkyl radicals may be saturated or unsaturated, branched or unbranched and may be singly or multiply  $R^{56}$  substituted, where

$R^{56}$  in each occurrence is the same or different and denotes hydroxyl, formyl, carboxyl, esters or salts thereof, carbamoyl, sulfo, esters or salts thereof, sulfamoyl, nitro, amino, phenyl,  $C_1$ - $C_5$ -alkyl or  $C_1$ - $C_5$ -alkoxy, and

the radicals  $R^{57}$  and  $R^{58}$  are the same or different and denote halogen or carboxyl and also esters or salts thereof, or have the meanings defined for  $R^{55}$ , or are linked together to form a  $[-CR^{61}R^{62}]_n$  ring, where n is 2, 3 or 4, and

$R^{59}$  and  $R^{60}$  have the meanings defined for  $R^{55}$ , and

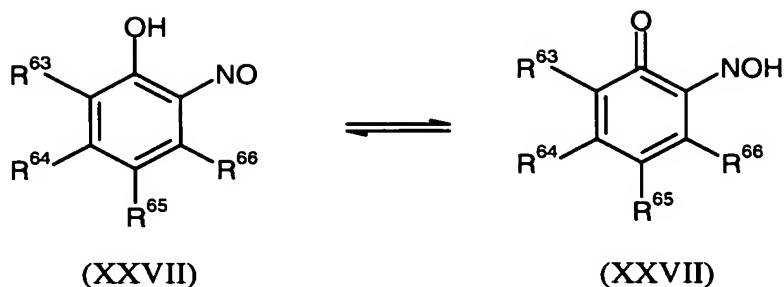
$R^{61}$  and  $R^{62}$  are the same or different and denote halogen or carboxyl and also esters or salts thereof, or have the meanings defined for  $R^{55}$ .

Particular preference for use as mediators is given to compounds having the general formula (XXIV) wherein U denotes oxygen or sulfur and the remaining radicals are each as defined above. Dimethyl 2-hydroxyiminomalonate is an example of such a compound.

Particular preference for use as mediators is further given to **isonitroso derivatives of cyclic ureides** of the general formula (XXV). Examples of such compounds are 1-methylvioluric acid, 1,3-dimethylvioluric acid, thiovioluric acid, alloxane-4,5-dioxime.

Especial preference for use as a mediator is given to alloxane-5-oxime hydrate (violuric acid) and/or its esters, ethers or salts.

The mediator may further be selected from the group of vicinally nitroso-substituted aromatic alcohols of the general formulae (XXVI) or (XXVII)



and also salts, ethers or esters thereof, where

5

$\text{R}^{63}$ ,  $\text{R}^{64}$ ,  $\text{R}^{65}$  and  $\text{R}^{66}$  are the same or different and denote hydrogen, halogen, hydroxyl, formyl, carbamoyl or carboxyl and also esters or salts thereof, sulfo, esters or salts thereof, sulfamoyl, nitro, nitroso, cyano, amino, phenyl, aryl- $\text{C}_1\text{-C}_5$ -alkyl,  $\text{C}_1\text{-C}_{12}$ -alkyl,  $\text{C}_1\text{-C}_5$ -alkoxy,  $\text{C}_1\text{-C}_{10}$ -carbonyl, carbonyl- $\text{C}_1\text{-C}_6$ -alkyl, phospho, 10 phosphono or phosphonooxy and also esters or salts thereof, where the carbamoyl, sulfamoyl, amino and phenyl radicals may be unsubstituted or singly or multiply  $\text{R}^{67}$  substituted and the aryl- $\text{C}_1\text{-C}_5$ -alkyl,  $\text{C}_1\text{-C}_{12}$ -alkyl,  $\text{C}_1\text{-C}_5$ -alkoxy,  $\text{C}_1\text{-C}_{10}$ -carbonyl, carbonyl- $\text{C}_1\text{-C}_6$ -alkyl radicals may be saturated or unsaturated, branched or unbranched and may be singly or multiply  $\text{R}^{67}$  substituted, where

15

$\text{R}^{67}$  in each occurrence is the same or different and denotes hydroxyl, formyl or carboxyl and also esters or salts thereof, carbamoyl, sulfo and also salts or esters thereof, sulfamoyl, nitro, nitroso, amino, phenyl,  $\text{C}_1\text{-C}_5$ -alkyl or  $\text{C}_1\text{-C}_5$ -alkoxy or the  $\text{R}^{63}$ ,  $\text{R}^{64}$ ,  $\text{R}^{65}$  and  $\text{R}^{66}$  radicals are linked together pairwise to form a  $[-\text{CR}^{68}\text{R}^{69}-]_m$  20 ring, where  $m$  is an integer from 1 to 4, or to form a  $[-\text{CR}^{70}=\text{CR}^{71}-]_n$  ring, where  $n$  is an integer from 1 to 3, and

$\text{R}^{68}$ ,  $\text{R}^{69}$ ,  $\text{R}^{70}$  and  $\text{R}^{71}$  are the same or different and have the meanings defined for  $\text{R}^{63}$  to  $\text{R}^{66}$ .

25

Aromatic alcohols are preferably to be understood as meaning phenols or fused derivatives of phenol.

Preference for use as mediators is given to compounds of the general 30 formula (XXVI) or (XXVII) whose synthesis can be reduced to the nitrosation of

substituted phenols.

Examples of such compounds are:

- |    |                                    |
|----|------------------------------------|
| 5  | 2-Nitrosophenol,                   |
|    | 3-Methyl-6-nitrosophenol,          |
|    | 2-Methyl-6-nitrosophenol,          |
|    | 4-Methyl-6-nitrosophenol,          |
|    | 3-Ethyl-6-nitrosophenol,           |
| 10 | 2-Ethyl-6-nitrosophenol,           |
|    | 4-Ethyl-6-nitrosophenol,           |
|    | 4-Isopropyl-6-nitrosophenol,       |
|    | 4-tert-butyl-6-nitrosophenol,      |
|    | 2-Phenyl-6-nitrosophenol,          |
| 15 | 2-Benzyl-6-nitrosophenol,          |
|    | 4-Benzyl-6-nitrosophenol,          |
|    | 2-Hydroxy-3-nitrosobenzyl alcohol, |
|    | 2-Hydroxy-3-nitrosobenzoic acid,   |
|    | 4-Hydroxy-3-nitrosobenzoic acid,   |
| 20 | 2-Methoxy-6-nitrosophenol,         |
|    | 3,4-Dimethyl-6-nitrosophenol,      |
|    | 2,4-Dimethyl-6-nitrosophenol,      |
|    | 3,5-Dimethyl-6-nitrosophenol,      |
|    | 2,5-Dimethyl-6-nitrosophenol,      |
| 25 | 2-Nitrosoresorcinol,               |
|    | 4-Nitrosoresorcinol,               |
|    | 2-Nitrosoorcinol,                  |
|    | 2-Nitrosophloroglucine,            |
|    | 4-Nitrosopyrogallol,               |
| 30 | 4-Nitroso-3-hydroxyaniline,        |
|    | 4-Nitro-2-nitrosophenol.           |

Preference for use as mediators is further given to o-nitroso derivatives of fused aromatic alcohols.

Examples of such compounds are:

- 2-Nitroso-1-naphthol,  
1-Methyl-3-nitroso-2-naphthol,  
5 9-Hydroxy-10-nitroso-phenanthrene.

Particular preference for use as mediators is given to:

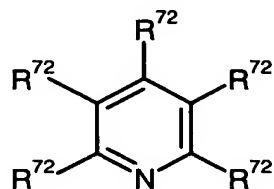
- 1-Nitroso-2-naphthol,  
10 1-Nitroso-2-naphthol-3,6-disulfonic acid,  
2-Nitroso-1-naphthol-4-sulfonic acid,  
2,4-Dinitroso-1,3-dihydroxybenzene

and also esters, ethers or salts thereof.

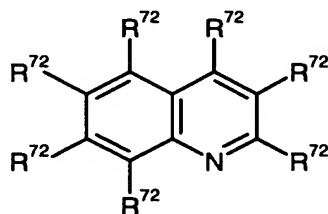
15

The mediator may further be selected from the group consisting of hydroxypyridines, aminopyridines, hydroxyquinolines, aminoquinolines, hydroxyisoquinolines, aminoisoquinolines, having nitroso or mercapto substituents ortho or para to the hydroxyl or amino groups, tautomers of the identified compounds and also their  
20 salts, ethers and esters.

Preference for use as mediators is given to compounds of the general formula (XXVIII), (XXIX) or (XXX)

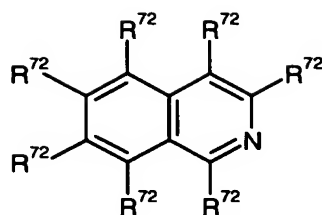


(XXVIII)



(XXIX)

25



(XXX)

and also tautomers, salts, ethers or esters thereof, where in the formulae (XXVIII), (XXIX) and (XXX) two mutually ortho- or para-disposed  $R^{72}$  radicals denote hydroxyl and nitroso or hydroxyl and mercapto or nitroso and amino and the other  $R^{72}$  radicals are the same or different and denote hydrogen, halogen, hydroxyl, mercapto, formyl, cyano, carbamoyl or carboxyl and also esters and salts thereof, sulfo, esters and salts thereof, sulfamoyl, nitro, nitroso, amino, phenyl, aryl- $C_1$ - $C_5$ -alkyl,  $C_1$ - $C_{12}$ -alkyl,  $C_1$ - $C_5$ -alkoxy,  $C_1$ - $C_{10}$ -carbonyl, carbonyl- $C_1$ - $C_6$ -alkyl, phospho, phosphono or phosphonooxy and also esters and salts thereof and where the carbamoyl, sulfamoyl, amino, mercapto and phenyl radicals may be unsubstituted or singly or multiply  $R^{73}$  substituted and the aryl- $C_1$ - $C_5$ -alkyl,  $C_1$ - $C_{12}$ -alkyl,  $C_1$ - $C_5$ -alkoxy,  $C_1$ - $C_{10}$ -carbonyl, carbonyl- $C_1$ - $C_6$ -alkyl radicals may be saturated or unsaturated, branched or unbranched and may be singly or multiply  $R^{73}$  substituted, where  $R^{73}$  in each occurrence is the same or different and denotes hydroxyl, formyl, cyano or carboxyl and also esters or salts thereof, carbamoyl, sulfo, sulfamoyl, nitro, nitroso, amino, phenyl,  $C_1$ - $C_5$ -alkyl,  $C_1$ - $C_5$ -alkoxy or  $C_1$ - $C_5$ -alkylcarbonyl and two  $R^{72}$  radicals at a time or two  $R^{73}$  radicals at a time or  $R^{72}$  and  $R^{73}$  may be linked together pairwise via a  $[-CR^{74}R^{75}-]_m$  bridge, where m is 1, 2, 3 or 4, and  $R^{74}$  and  $R^{75}$  are the same or different and denote carboxyl, esters or salts thereof, phenyl,  $C_1$ - $C_5$ -alkyl,  $C_1$ - $C_5$ -alkoxy or  $C_1$ - $C_5$ -alkylcarbonyl and one or more nonadjacent  $[-CR^{74}R^{75}-]$  groups may be replaced by oxygen or sulfur or an optionally  $C_1$ - $C_5$ -alkyl-substituted imino radical and two adjacent  $[-CR^{74}R^{75}-]$  groups may be replaced by one  $[-CR^{74}=R^{75}-]$  group.

25

Particular preference for use as mediators is given to compounds of the general formula (XXVIII) or (XXIX) and also their tautomers, salts, ethers or esters, where in the formulae (XXVIII) and (XXIX) two mutually ortho-disposed  $R^{72}$  radicals particularly preferably denote hydroxyl and nitroso or hydroxyl and mercapto or nitroso and amino and the other  $R^{72}$  radicals are the same or different and denote hydrogen, hydroxyl, mercapto, formyl, carbamoyl or carboxyl and also esters and

30

salts thereof, sulfo, esters and salts thereof, sulfamoyl, nitro, nitroso, amino, phenyl, aryl-C<sub>1</sub>-C<sub>5</sub>-alkyl, C<sub>1</sub>-C<sub>5</sub>-alkyl, C<sub>1</sub>-C<sub>5</sub>-alkoxy, C<sub>1</sub>-C<sub>5</sub>-carbonyl, carbonyl-C<sub>1</sub>-C<sub>6</sub>-alkyl, phospho, phosphono or phosphonooxy and also esters and salts thereof, where the carbamoyl, sulfamoyl, amino, mercapto and phenyl radicals may be unsubstituted or  
 5 singly or multiply R<sup>73</sup> substituted and the aryl-C<sub>1</sub>-C<sub>5</sub>-alkyl, C<sub>1</sub>-C<sub>5</sub>-alkyl, C<sub>1</sub>-C<sub>5</sub>-alkoxy, C<sub>1</sub>-C<sub>5</sub>-carbonyl, carbonyl-C<sub>1</sub>-C<sub>6</sub>-alkyl radicals may be saturated or unsaturated, branched or unbranched and may be singly or multiply R<sup>73</sup> substituted, where R<sup>73</sup> is as defined above and two R<sup>73</sup> radicals at a time may be linked together pairwise via a [-CR<sup>74</sup>R<sup>75</sup>-]<sub>m</sub> bridge, where m is 2, 3 or 4, and R<sup>74</sup> and R<sup>75</sup> are as  
 10 defined above and one or more nonadjacent [-CR<sup>74</sup>R<sup>75</sup>-] groups may be replaced by O or an optionally C<sub>1</sub>-C<sub>5</sub>-alkyl-substituted imino radical.

Examples of compounds useful as mediators are

- 15 2,6-Dihydroxy-3-nitrosopyridine,
- 2,3-Dihydroxy-4-nitrosopyridine,
- 2,6-Dihydroxy-3-nitrosopyridine-4-carboxylic acid,
- 2,4-Dihydroxy-3-nitrosopyridine,
- 3-Hydroxy-2-mercaptopyridine,
- 20 2-Hydroxy-3-mercaptopyridine,
- 2,6-Diamino-3-nitrosopyridine,
- 2,6-Diamino-3-nitroso-pyridine-4-carboxylic acid,
- 2-Hydroxy-3-nitrosopyridine,
- 3-Hydroxy-2-nitrosopyridine,
- 25 2-Mercapto-3-nitrosopyridine,
- 3-Mercapto-2-nitrosopyridine,
- 2-Amino-3-nitrosopyridine,
- 3-Amino-2-nitrosopyridine,
- 2,4-Dihydroxy-3-nitrosoquinoline,
- 30 8-Hydroxy-5-nitroisoquinoline,
- 2,3-Dihydroxy-4-nitrosoquinoline,
- 3-Hydroxy-4-nitrosoisoquinoline,
- 4-Hydroxy-3-nitrosoisoquinoline,
- 8-Hydroxy-5-nitrosoisoquinoline

and also tautomers of these compounds.

Preference for use as mediators is given to

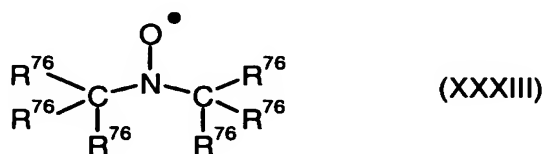
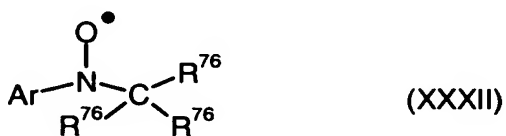
- 5            2,6-Dihydroxy-3-nitrosopyridine,  
               2,6-Diamino-3-nitrosopyridine,  
               2,6-Dihydroxy-3-nitrosopyridine-4-carboxylic acid,  
               2,4-Dihydroxy-3-nitrosopyridine,  
               2-Hydroxy-3-mercaptopyridine,  
 10           2-Mercapto-3-pyridinol,  
               2,4-Dihydroxy-3-nitrosoquinoline,  
               8-Hydroxy-5-nitrosoquinoline,  
               2,3-Dihydroxy-4-nitrosoquinoline

- 15          and also tautomers of these compounds.

The mediator may further be selected from the group of **stable nitroxyl free radicals** (nitroxides), i.e., these free radicals can be obtained, characterized and stored in pure form.

20

Preference for use as mediators is given in this connection to compounds of the general formula (XXXI), (XXXII) or (XXXIII)



where

Ar is a univalent homo- or heteroaromatic mono- or binuclear radical and where this aromatic radical may be substituted by one or more, identical or different  $R^{77}$  radicals, where  $R^{77}$  denotes halogen, formyl, cyano, carbamoyl, carboxyl, esters or salts thereof, sulfo, esters or salt thereof, sulfamoyl, nitro, nitroso, amino, phenyl, aryl- $C_1$ - $C_5$ -alkyl,  $C_1$ - $C_{12}$ -alkyl,  $C_1$ - $C_5$ -alkoxy,  $C_1$ - $C_{10}$ -carbonyl, carbonyl- $C_1$ - $C_6$ -alkyl, phospho, phosphono or phosphonooxy and also esters or salts thereof, and

where the phenyl, carbamoyl and sulfamoyl radicals may be unsubstituted or singly or multiply  $R^{78}$  substituted, the amino radical may be singly or doubly  $R^{78}$  substituted and the aryl- $C_1$ - $C_5$ -alkyl,  $C_1$ - $C_{12}$ -alkyl,  $C_1$ - $C_5$ -alkoxy,  $C_1$ - $C_{10}$ -carbonyl, carbonyl- $C_1$ - $C_6$ -alkyl radicals may be saturated or unsaturated, branched or unbranched and may be singly or multiply  $R^{78}$  substituted,

where  $R^{78}$  may occur one or more times and in each occurrence is the same or different and denotes hydroxyl, formyl, cyano, carboxyl and also esters or salts thereof, carbamoyl, sulfo, sulfamoyl, nitro, nitroso, amino, phenyl,  $C_1$ - $C_5$ -alkyl,  $C_1$ - $C_5$ -alkoxy or  $C_1$ - $C_5$ -alkylcarbonyl, and

$R^{76}$  in each occurrence is the same or different and denotes halogen, hydroxyl, mercapto, formyl, cyano, carbamoyl, carboxyl and also esters or salts thereof, sulfo, esters or salts thereof, sulfamoyl, nitro, nitroso, amino, phenyl, aryl- $C_1$ - $C_5$ -alkyl,  $C_1$ - $C_{12}$ -alkyl,  $C_1$ - $C_5$ -alkoxy,  $C_1$ -10-carbonyl, carbonyl- $C_1$ - $C_6$ -alkyl, phospho, phosphono or phosphonooxy and also esters or salts thereof, and

$R^{76}$  may also denote hydrogen in the case of bicyclic stable nitroxyl free radicals (structure XXXIII), and

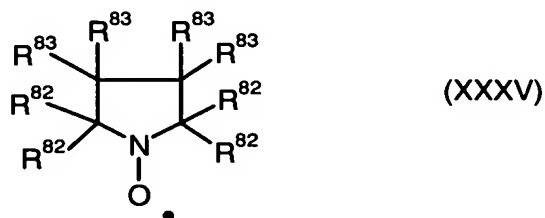
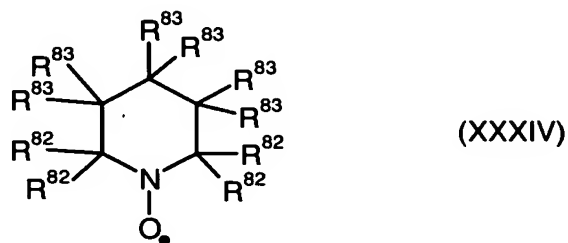
where the carbamoyl, sulfamoyl, amino, mercapto and phenyl radicals may be unsubstituted or singly or multiply  $R^{79}$  substituted and the aryl- $C_1$ - $C_5$ -alkyl,  $C_1$ - $C_{12}$ -alkyl,  $C_1$ - $C_5$ -alkoxy,  $C_1$ - $C_{10}$ -carbonyl, carbonyl- $C_1$ - $C_6$ -alkyl radicals may be saturated or unsaturated, branched or unbranched and may be singly or multiply  $R^{79}$  substituted, where  $R^{79}$  in each occurrence is the same or different and denotes hydroxyl, formyl, cyano, carboxyl, esters or salts thereof, carbamoyl, sulfo, esters and salts thereof, sulfamoyl, nitro, nitroso, amino, phenyl,  $C_1$ - $C_5$ -alkyl,  $C_1$ - $C_5$ -alkoxy

or C<sub>1</sub>-C<sub>5</sub>-alkylcarbonyl and two R<sup>78</sup> or R<sup>79</sup> radicals at a time may be linked together pairwise via a [-CR<sup>80</sup>R<sup>81</sup>-]<sub>m</sub> bridge, where m is 0, 1, 2, 3 or 4, and

R<sup>80</sup> and R<sup>81</sup> are the same or different and denote halogen, carboxyl and also esters or salts thereof, carbamoyl, sulfamoyl, phenyl, benzoyl, C<sub>1</sub>-C<sub>5</sub>-alkyl, C<sub>1</sub>-C<sub>5</sub>-alkoxy or C<sub>1</sub>-C<sub>5</sub>-alkylcarbonyl and one or more nonadjacent [-CR<sup>80</sup>R<sup>81</sup>-] groups may be replaced by oxygen or sulfur or an optionally C<sub>1</sub>-C<sub>5</sub>-alkyl-substituted imino radical and two adjacent [-CR<sup>80</sup>R<sup>81</sup>-] groups may be replaced by one [-CR<sup>80</sup>=CR<sup>81</sup>-], [-CR<sup>80</sup>=N-] or [-CR<sup>80</sup>=N(O)-] group.

10

Particular preference for use as mediators is given to nitroxyl free radicals of the general formulae (XXXIV) and (XXXV)



15

where

R<sup>82</sup> in each occurrence is the same or different and denotes phenyl, aryl-C<sub>1</sub>-C<sub>5</sub>-alkyl, C<sub>1</sub>-C<sub>12</sub>-alkyl, C<sub>1</sub>-C<sub>5</sub>-alkoxy, C<sub>1</sub>-C<sub>10</sub>-carbonyl or carbonyl-C<sub>1</sub>-C<sub>6</sub>-alkyl, where the phenyl radicals may be unsubstituted or singly or multiply R<sup>84</sup> substituted and the aryl-C<sub>1</sub>-C<sub>5</sub>-alkyl, C<sub>1</sub>-C<sub>12</sub>-alkyl, C<sub>1</sub>-C<sub>5</sub>-alkoxy, C<sub>1</sub>-C<sub>10</sub>-carbonyl and carbonyl-C<sub>1</sub>-C<sub>6</sub>-alkyl radicals may be saturated or unsaturated, branched or unbranched and may be singly or multiply R<sup>84</sup> substituted, where R<sup>84</sup> may occur one or more times and in each occurrence is the same or different and denotes hydroxyl, formyl or carboxyl and also esters or salts thereof, carbamoyl, sulfo, esters and salts thereof, sulfamoyl,

25

nitro, nitroso, amino, phenyl, benzoyl, C<sub>1</sub>-C<sub>5</sub>-alkyl, C<sub>1</sub>-C<sub>5</sub>-alkoxy or C<sub>1</sub>-C<sub>5</sub>-alkylcarbonyl, and

R<sup>83</sup> in each occurrence is the same or different and denotes hydrogen, hydroxyl,  
 5 mercapto, formyl, cyano, carbamoyl, carboxyl and also esters or salts thereof, sulfo  
 and also esters or salts thereof, sulfamoyl, nitro, nitroso, amino, phenyl,  
 aryl-C<sub>1</sub>-C<sub>5</sub>-alkyl, C<sub>1</sub>-C<sub>12</sub>-alkyl, C<sub>1</sub>-C<sub>5</sub>-alkoxy, C<sub>1</sub>-C<sub>10</sub>-carbonyl, carbonyl-C<sub>1</sub>-C<sub>6</sub>-alkyl,  
 phospho, phosphono or phosphonooxy and also esters or salts thereof, where the  
 carbamoyl, sulfamoyl, amino, mercapto and phenyl radicals may be unsubstituted or  
 10 singly or multiply R<sup>78</sup> substituted and the aryl-C<sub>1</sub>-C<sub>5</sub>-alkyl, C<sub>1</sub>-C<sub>12</sub>-alkyl,  
 C<sub>1</sub>-C<sub>5</sub>-alkoxy, C<sub>1</sub>-C<sub>10</sub>-carbonyl and carbonyl-C<sub>1</sub>-C<sub>6</sub>-alkyl radicals may be saturated  
 or unsaturated, branched or unbranched and may be singly or multiply R<sup>78</sup>  
 substituted and one [-CR<sup>83</sup>R<sup>83</sup>-] group may be replaced by oxygen, an optionally  
 C<sub>1</sub>-C<sub>5</sub>-alkyl-substituted imino radical, a (hydroxy)imino radical, a carbonyl function  
 15 or an optionally R<sup>78</sup> mono- or disubstituted vinylidene function and two adjacent  
 [-CR<sup>83</sup>R<sup>83</sup>-] groups may be replaced by one [-CR<sup>83</sup>-CR<sup>83</sup>-] or [-CR<sup>83</sup>=N-] or  
 [-CR<sup>83</sup>=N(O)-] group.

Examples of compounds useful as mediators are

20

2,2,6,6-Tetramethyl-1-piperidinyloxy free radical (TEMPO),  
 4-Hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxy free radical,  
 4-Oxo-2,2,6,6-tetramethyl-1-piperidinyloxy free radical,  
 4-Acetamido-2,2,6,6-tetramethyl-1-piperidinyloxy free radical,  
 25 4-(Ethoxyfluorophosphinyloxy)-2,2,6,6-tetramethyl-1-piperidinyloxy free  
 radical,  
 4-(Isothiocyanato)-2,2,6,6-tetramethyl-1-piperidinyloxy free radical,  
 4-Maleimido-2,2,6,6-tetramethyl-1-piperidinyloxy free radical,  
 4-(4-Nitrobenzoyloxy)-2,2,6,6-tetramethyl-1-piperidinyloxy free radical,  
 30 4-(Phosphonooxy)-2,2,6,6-tetramethyl-1-piperidinyloxy free radical,  
 4-Cyano-2,2,6,6-tetramethyl-1-piperidinyloxy free radical,  
 3-Carbamoyl-2,2,5,5-tetramethyl-3-pyrrolinyl-1-oxy free radical,  
 4-Phenyl-2,2,5,5-tetramethyl-3-imidazolin-1-yloxy 3-oxide free radical,  
 4-Carbamoyl-2,2,5,5-tetramethyl-3-imidazolin-1-yloxy 3-oxide free radical,

- 4-Phenacylidene-2,2,5,5-tetramethyl-1-imidazolidinyloxy,  
 3-(Aminomethyl)-2,2,5,5-tetramethyl-N-pyrrolidinyloxy,  
 3-Carbamoyl-2,2,5,5-tetramethyl-N-pyrrolidinyloxy,  
 3-Carboxy-2,2,5,5-tetramethyl-N-pyrrolidinyloxy,  
 5 3-Cyano-2,2,5,5-tetramethyl-N-pyrrolidinyloxy,  
 3-Maleimido-2,2,5,5-tetramethyl-N-pyrrolidinyloxy and  
 3-(4-Nitrophenoxycarbonyl)-2,2,5,5-tetramethyl-N-pyrrolidinyloxy.

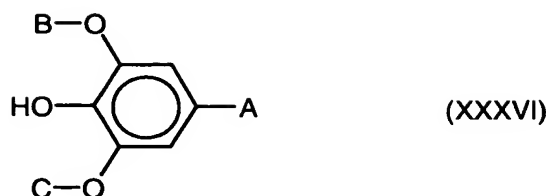
Preference for use as mediators is given to

- 10 2,2,6,6-Tetramethyl-1-piperidinyloxy free radical (TEMPO),  
 4-Hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxy free radical,  
 4-Oxo-2,2,6,6-tetramethyl-1-piperidinyloxy free radical,  
 4-Acetamido-2,2,6,6-tetramethyl-1-piperidinyloxy free radical,  
 15 4-(Isothiocyanato)-2,2,6,6-tetramethyl-1-piperidinyloxy free radical,  
 4-Maleimido-2,2,6,6-tetramethyl-1-piperidinyloxy free radical,  
 4-(4-Nitrobenzoyloxy)-2,2,6,6-tetramethyl-1-piperidinyloxy free radical,  
 4-(Phosphonooxy)-2,2,6,6-tetramethyl-1-piperidinyloxy free radical,  
 4-Cyano-2,2,6,6-tetramethyl-1-piperidinyloxy free radical,  
 20 3-Carbamoyl-2,2,5,5-tetramethyl-3-pyrrolinyl-1-oxy free radical,  
 4-Phenyl-2,2,5,5-tetramethyl-3-imidazolin-1-yloxy 3-oxide free radical,  
 4-Carbamoyl-2,2,5,5-tetramethyl-3-imidazolin-1-yloxy 3-oxide free radical,  
 4-Phenacylidene-2,2,5,5-tetramethyl-1-imidazolidinyloxy.

- 25 Special preference for use as mediators is given to

2,2,6,6-Tetramethyl-1-piperidinyloxy free radical (TEMPO) and  
 4-Hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxy free radical.

- 30 Useful mediators further include compounds of the general formula (XXXVI):



where

A denotes a  $-D$ ,  $-\text{CH}=\text{CH}-D$ ,  $-\text{CH}=\text{CH}-\text{CH}=\text{CH}-D$ ,  $-\text{CH}=\text{N}-D$ , or  $-\text{N}=\text{CH}-D$  group, where D denotes a  $-\text{CO}-E$ ,  $-\text{SO}_2-E$ ,  $-\text{N}-\text{XY}$  or  $-\text{N}^+-\text{XYZ}$  group wherein E denotes either hydrogen, hydroxyl, a  $-\text{R}$  or  $-\text{OR}$  radical and X, Y and Z are the same or different and hydrogen or a  $-\text{R}$  radical, where R is a  $\text{C}_1$ - $\text{C}_{16}$ -alkyl radical, preferably a  $\text{C}_1$ - $\text{C}_8$ -alkyl radical, and alkyl is in each case saturated or unsaturated, straight-chain or branched and optionally carboxyl, sulfo or amino substituted; and

B and C are the same or different and represent a  $\text{C}_m\text{H}_{2m+1}$  group where  $1 \leq m \leq 5$ .

In one preferred embodiment A in the general formula (XXXVI) represents a  $-\text{CO}-E$  group wherein E is hydrogen, hydroxyl, a  $-\text{R}$  or  $-\text{OR}$  radical, wherein R is a  $\text{C}_1$ - $\text{C}_{16}$ -alkyl radical and preferably a  $\text{C}_1$ - $\text{C}_8$ -alkyl radical, and alkyl is in each case saturated or unsaturated, straight-chain or branched and optionally substituted by a carboxyl, sulfo or amino group and B and C are the same or different and signify a group  $\text{C}_m\text{H}_{2m+1}$  where  $1 \leq m \leq 5$ .

In the general formula (XXXVI), A may also be situated in meta to the hydroxyl group instead of being disposed in the para position as shown in the formula (XXXVI).

Particular preference is given to mediators of the general formula (XXXVI) which are acetosyringon (3,5-dimethoxy-4-hydroxyacetophenone), methyl syringate, ethyl syringate, propyl syringate, butyl syringate, hexyl syringate or octyl syringate.

In summary, the following mediators are particularly preferred:

- 3-Amino-N-hydroxyphthalimide,  
4-Amino-N-hydroxyphthalimide,  
N-Hydroxyphthalimide,  
3-Hydroxy-N-hydroxyphthalimide,  
5 3-Methoxy-N-hydroxyphthalimide,  
3,4-Dimethoxy-N-hydroxyphthalimide,  
4,5-Dimethoxy-N-hydroxyphthalimide,  
3,6-Dihydroxy-N-hydroxyphthalimide,  
3,6-Dimethoxy-N-hydroxyphthalimide,  
10 3-Methyl-N-hydroxyphthalimide,  
4-Methyl-N-hydroxyphthalimide,  
3,4-Dimethyl-N-hydroxyphthalimide,  
3,5-Dimethyl-N-hydroxyphthalimide,  
3,6-Dimethyl-N-hydroxyphthalimide,  
15 3-Isopropyl-6-methyl-N-hydroxyphthalimide,  
3-Nitro-N-hydroxyphthalimide,  
4-Nitro-N-hydroxyphthalimide,  
1-Hydroxybenzotriazole and its salts,  
1-Hydroxybenzotriazole-4-sulfonic acid and salts thereof,  
20 1-Hydroxybenzotriazole-5-sulfonic acid and salts thereof,  
1-Hydroxybenzotriazole-6-sulfonic acid and salts thereof,  
1-Hydroxybenzotriazole-7-sulfonic acid and salts thereof,  
1-Hydroxybenzotriazole-4-carbonic acid and salts thereof,  
1-Hydroxybenzotriazole-5-carbonic acid and salts thereof,  
25 1-Hydroxybenzotriazole-6-carbonic acid and salts thereof,  
1-Hydroxybenzotriazole-7-carbonic acid and salts thereof,  
Violuric acid,  
N-Hydroxyacetanilide,  
3-Nitrosoquinoline-2,4-diol,  
30 2,4-Dihydroxy-3-nitrosopyridine,  
2,6-Dihydroxy-3-nitrosopyridine,  
2,4-Dinitroso-1,3-dihydroxybenzene,  
2-Nitroso-1-naphthol-3-sulfonic acid,

1-Nitroso-2-naphthol-3,6-disulfonic acid, and  
Methyl syringate.

Very particularly preferred mediators are:

5

N-Hydroxyphthalimide,  
1-Hydroxybenzotriazole,  
1-Hydroxybenzotriazole-6-sulfonic acid and salts thereof  
Methyl syringate

10

Violuric acid,  
N-Hydroxyacetanilide,  
Nitrosonaphthols,  
Nitrosopyridinols and their above-recited derivatives.

15 The macrocyclic metal complex is used in the inventively used oxidizing system in an amount in the range from 0.01  $\mu\text{M}$  to 1000  $\mu\text{M}$ . Preference is given to an amount in the range from 0.1  $\mu\text{M}$  to 100  $\mu\text{M}$ .

20 The oxidizing agent is used in the inventively used oxidizing system in an amount in the range of 0.01-1000 mM. Preference is given to an amount in the range of 0.1-100 ppm.

25 The oxidation-enhancing compound is used in the oxidizing system of the invention in an amount in the range from 0.1  $\mu\text{M}$ -50 mM. The range of 1  $\mu\text{M}$ -1 mM is preferred. The range from 10  $\mu\text{M}$ -0.5 mM is particularly preferred.

30 The invention further provides a process for oxidizing oxidizable substances which is characterized in that the oxidizable substance is contacted with a specific oxidizing system, the specific oxidizing system comprising a macrocyclic metal complex, an oxidizing agent and an oxidation-enhancing compound as defined above.

The oxidizing system of the invention is used for example in the following oxidation reactions:

- to remove colored impurities from industrial wastewater, preferably from wastewater of the paper- or textile-processing industry,
- 5       • to lighten colored impurities on solid materials, preferably on textiles, paper or leather,
- to decolorize excess, unfixed dyes from dyed textile materials,
- 10       • to inhibit unwanted mutual dye transfer during the washing of differently dyed textiles.

The invention accordingly further provides a process for removing excess, unfixed dye from textile materials after a dyeing, preferably after a reactive dyeing, the process being characterized in that the dyed textile material is contacted with the  
15       oxidizing system of the invention in at least one of the post-dyeing rinse steps.

It is advantageous that this process makes it possible to remove excess, unfixed dye from the textile without decolorizing the dyed textile itself.

20       The coloring of the textile material can be through dyeing or printing and will hereinafter be collectively referred to as "dyeing".

Preferably, the dyed textile material is contacted with the oxidizing system of the invention in at least one of the post-dyeing rinse steps by at least one of the rinse  
25       liquors having added to it

- 1)       the three components of the oxidizing system individually in any desired order in succession or else individually and concurrently, or
- 30       2)       initially the two components of the macrocyclic metal complex and of the oxidation-enhancing compound either individually and concurrently or else as a conjoint formulation and subsequently the oxidizing agent or

3) initially the two components of the oxidizing agent and of the oxidation-enhancing compound either individually and concurrently or else as a conjoint formulation and subsequently the macrocyclic metal complex.

5 In the abovementioned variant 1, at least one of the rinse liquors and preferably one rinse liquor has all three components of the oxidizing system added to it individually in any desired order in succession or else individually and concurrently.

10 In the abovementioned variant 2, at least one of the rinse liquors and preferably one rinse liquor initially has the two components of the macrocyclic metal complex and of the oxidation-enhancing compound added to it either individually and concurrently or else as a conjoint formulation before the oxidizing agent is added.

15 In this variant 2, it is advantageous to ensure thorough mixing through of the system after the addition of the two components of the macrocyclic metal complex and of the oxidation-enhancing compound. The oxidative decolorization is subsequently started by the addition of the oxidizing agent. On conclusion of the decolorization, the rinse liquor is dropped and the textile is if appropriate washed a further time with water.

20 In the abovementioned variant 3, initially the two components of the oxidizing agent and of the oxidation-enhancing compound are added either individually and concurrently or else as a conjoint formulation before the macrocyclic metal complex is added.

25 Again, a short phase of mixing through before the macrocyclic metal complex is added will prove advantageous.

30 When the macrocyclic metal complex is added individually in the three variants mentioned above, it is typically added in the form of an aqueous solution to which may optionally have been added 0.5-40% by weight, based on the entire solution, of a pH stabilizer and of a water-soluble or at least partially water-soluble solvent. As suitable water-soluble solvents there may be mentioned ethanol, methanol, isopropanol, ethylene glycol, diethylene glycol, polyethylene glycols, ethylene glycol

monoethyl ether, ethylene glycol monomethyl ether, diethylene glycol monobutyl ether, acetone, acetonitrile, acetamide, tetrahydrofuran, dioxane, dimethyl sulfoxide, dimethylformamide, sulfolane or mixtures thereof. Suitable pH stabilizers are phosphate, citrate buffer, carbonate buffer or borate buffer, or mixtures thereof.

5

When hydrogen peroxide is used as oxidizing agent, it is used in the form of for example commercially available aqueous solutions having an assay of 3-50%.

When the oxidation-enhancing compound is added individually in the three variants mentioned above, it can be added to the rinse liquor in solid form. But it is possible and preferable to add the oxidation-enhancing compound in the form of a dispersion or solution, more preferably in the form of an aqueous solution to which may optionally have been added 0.5-40% by weight, based on the entire solution, of a pH stabilizer and of a water-soluble or at least partially water-soluble solvent. As suitable water-soluble solvents there may be mentioned ethanol, methanol, isopropanol, ethylene glycol, diethylene glycol, polyethylene glycols, ethylene glycol monoethyl ether, ethylene glycol monomethyl ether, diethylene glycol monobutyl ether, acetone, acetonitrile, acetamide, tetrahydrofuran, dioxane, dimethyl sulfoxide, dimethylformamide, sulfolane or mixtures thereof. Suitable pH stabilizers are phosphate, citrate buffer, carbonate buffer or borate buffer, or mixtures thereof.

When, as per variant 2, the macrocyclic metal complex and the oxidation-enhancing compound are used in a conjoint, preferably aqueous formulation, this aqueous formulation will include the macrocyclic metal complex in a concentration of 0.01-100 mM and the oxidation-enhancing compound in a concentration of 1-1000 mM.

When, as per variant 3, the oxidizing agent and the oxidation-enhancing compound are used in a conjoint, preferably aqueous formulation, this aqueous formulation will include the oxidizing agent in a concentration of 0.1-20% by weight and the oxidation-enhancing compound in a concentration of 0.1-20% by weight.

These aqueous formulations of macrocyclic metal complex and oxidation-enhancing compound (variant 2) or of oxidizing agent and oxidation-enhancing compound

(variant 3) are prepared by mixing the two respective components of the oxidizing system of the invention and also if appropriate one or more of the hereinbelow identified additives in any order using water as a solvent.

- 5 Useful additives include deterative substances, preferably surfactants, sequestrants, defoamers, enzymes, such as amylases, pectinases, proteases, peroxidase, laccases or lipases, water-conditioning agents, such as water softeners, pH stabilizers, such as phosphate, citrate buffer, carbonate buffer or borate buffer, or mixtures thereof, or solvents which are soluble or at least partially soluble in water. Suitable water-  
10 soluble solvents are ethanol, methanol, isopropanol, ethylene glycol, diethylene glycol, polyethylene glycols, ethylene glycol monoethyl ether, ethylene glycol monomethyl ether, diethylene glycol monobutyl ether, acetone, acetonitrile, acetamide, tetrahydrofuran, dioxane, dimethyl sulfoxide, dimethylformamide, sulfolane or mixtures thereof.

- 15 Such additives are used at 0-50% by weight and preferably 0.01-30% by weight, based on the entire formulation.

- It is particularly preferable for the oxidizing system of the invention to be contacted  
20 with the textile in one of the post-dyeing rinse steps according to one of the three variants identified above.

- The treatment time using the oxidizing system of the invention depends on the type and amount of excess dye to be decolorized. Generally, 2-60 min are sufficient. If  
25 appropriate, a further addition of either any one or all of the components of the oxidizing system of the invention can be advantageous during the treatment.

- The dyed textile materials may be cotton, filament viscose, staple viscose, lyocell, wool, silk, polyester, polyamide, polyacrylonitrile and elastane or blends thereof. The  
30 dyed textile materials are more preferably cotton, filament viscose and lyocell or blends thereof with polyester, polyamide or elastane.

The dyeing may be a dyeing with any commercially available dye. Useful dyes include reactive dyes, direct dyes, substantive dyes, acid dyes, metal complex dyes, disperse dyes, vat dyes and sulfur dyes.

- 5 The dyeings in question are preferably dyeings with water-soluble dyes and more preferably dyeings with reactive dyes.

The process for removing excess, unfixed dye is typically carried out at a temperature of 25-95°C and preferably carried out at a temperature of 40-80°C. The  
10 pH in the rinse liquor is in the range of 4-13, preferably 5-12 and more preferably 7-11.

The invention further provides a process for removing colored impurities from  
15 industrial wastewater, preferably from wastewater of the paper- or textile-processing industry, the process being characterized in that the industrial wastewater is contacted with the oxidizing system of the invention.

Preferably, the industrial wastewater is contacted with the oxidizing system of the  
20 invention by adding to the industrial wastewater

- 1) the three components of the oxidizing system individually in any desired order in succession or else individually and concurrently, or
- 25 2) initially the two components of the macrocyclic metal complex and of the oxidation-enhancing compound either individually and concurrently or else as a conjoint formulation and subsequently the oxidizing agent or
- 30 3) initially the two components of the oxidizing agent and of the oxidation-enhancing compound either individually and concurrently or else as a conjoint formulation and subsequently the macrocyclic metal complex.

The addition of the oxidizing system to the wastewater is in principle subject to the same remarks as the previously described variants 1-3 of the process for removing excess, unfixed dye from textile materials after a dyeing.

- 5     The treatment time of the industrial wastewater depends on the type and severity of contamination. Generally, 2-60 min are sufficient. If appropriate, a further addition of either any one or all of the components of the oxidizing system of the invention can be helpful during the treatment.
- 10    The process for removing colored impurities in industrial wastewaters is typically carried out at a temperature of 25-95°C and preferably carried out at a temperature of 40-80°C. The pH in the wastewater is in the range of 4-13, preferably 5-12 and more preferably 7-11.
- 15    The invention further provides a process for lightening colored impurities on solid materials, preferably on textiles, paper or leather, the process being characterized in that the solid materials are contacted with the oxidizing system of the invention.

- 20    These colored impurities are impurities and stains which are not attributable to dye as were described for the abovementioned process for removing excess dye from dyed textiles.

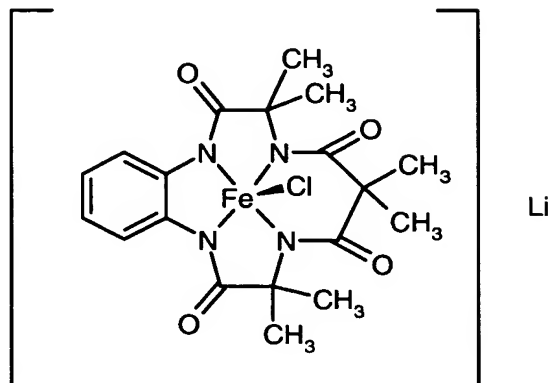
Preferably, the solid material is contacted with the oxidizing system of the invention by introducing the solid material into an aqueous liquor and adding

- 25
- 1)     the three components of the oxidizing system individually in any desired order in succession or else individually and concurrently, or
- 2)     initially the two components of the macrocyclic metal complex and of the
- 30     oxidation-enhancing compound either individually and concurrently or else as a conjoint formulation and subsequently the oxidizing agent or

- 3) initially the two components of the oxidizing agent and of the oxidation-enhancing compound either individually and concurrently or else as a conjoint formulation and subsequently the macrocyclic metal complex.
- 5 The addition of the oxidizing system to the aqueous liquor holding the material to be lightened is in principle subject to the same remarks as the previously described variants 1-3 of the process for removing excess, unfixed dye from textile materials after a dyeing.
- 10 The treatment time of the liquor of the material to be lightened depends on the type and severity of contamination to be lightened. Generally, 2-60 min are sufficient. If appropriate, a further addition of either any one or all of the components of the oxidizing system of the invention can be helpful during the treatment.
- 15 The process for lightening colored impurities on solid materials is typically carried out at a temperature of 25-95°C and preferably carried out at a temperature of 40-80°C. The pH in the aqueous liquor is in the range of 4-13, preferably 5-12 and more preferably 7-11.

**Examples**

The examples utilize a macrocyclic metal complex



- 5 which is prepared by the method described in Examples 1-6 of WO-A-02/16330. This compound is hereinbelow referred to as **1b**.

**Examples 1-7:**

- 10 The advantageous effect of the oxidizing system according to the invention is demonstrated using the decolorization of various dyes as an example. The “decolorization” is reported in the examples in terms of the percentage decrease in absorbance (= coloredness) measured at the absorbance peak. The higher the reported percentage, the better the decolorization. The tests are performed by adding
- 15 in succession with stirring the macrocyclic metal complex, the oxidation-enhancing compound and the oxidizing agent to an initial charge of the aqueous dye solution.

- The dye solution contains 30 mg/l of dye, the pH is set by a phosphate or borate buffer. The decolorization is monitored via a spectrophotometer. The various dye
- 20 types of the Remazol® and Levafix® series are dyes from DyStar GmbH Deutschland Co & KG.

The oxidizing system utilizes the following concentrations, based on the solution to be decolorized:

Compound **1b** = 1  $\mu$ M

Hydrogen peroxide = 2 mM

Oxidation-enhancing compound = 100  $\mu$ M

5 **Example 1:**

Decolorization of **Levafix Brilliant Red E-BA** after 10 min at pH = 9.0 and 25°C

Example	Components in oxidizing system	Absorbance (%)
Comparison	<b>1b</b> + H <sub>2</sub> O <sub>2</sub>	30
1-1	<b>1b</b> + H <sub>2</sub> O <sub>2</sub> + HOBT	99
1-2	<b>1b</b> + H <sub>2</sub> O <sub>2</sub> + violuric acid	94
1-3	<b>1b</b> + H <sub>2</sub> O <sub>2</sub> + methyl syringate	82

10 **Example 2:**

Decolorization of **Levafix Brilliant Red E-BA** after 10 min at pH = 8.3 and 25°C

Example	Components in oxidizing system	Absorbance (%)
Comparison	<b>1b</b> + H <sub>2</sub> O <sub>2</sub>	43
2-1	<b>1b</b> + H <sub>2</sub> O <sub>2</sub> + HOBT	99

15 **Example 3:**

Decolorization of **Remazol Brilliant Yellow 4GL** after 10 min at pH = 7.0 and 25°C

Example	Components in oxidizing system	Absorbance (%)
Comparison	<b>1b</b> + H <sub>2</sub> O <sub>2</sub>	2
3-1	<b>1b</b> + H <sub>2</sub> O <sub>2</sub> + violuric acid	18
3-2	<b>1b</b> + H <sub>2</sub> O <sub>2</sub> + methyl syringate	25

**Example 4:**

Decolorization of **Remazol Brilliant Yellow 4GL** after 10 min at pH = 8.3 and 25°C

Example	Components in oxidizing system	Absorbance (%)
Comparison	<u>1b</u> + H <sub>2</sub> O <sub>2</sub>	35
4-1	<u>1b</u> + H <sub>2</sub> O <sub>2</sub> + HOBT	63

5

**Example 5:**

Decolorization of **Remazol Brilliant Yellow 4GL** after 10 min at pH = 9.0 and 25°C

Example	Components in oxidizing system	Absorbance (%)
Comparison	<u>1b</u> + H <sub>2</sub> O <sub>2</sub>	37
5-1	<u>1b</u> + H <sub>2</sub> O <sub>2</sub> + HOBT	66
5-2	<u>1b</u> + H <sub>2</sub> O <sub>2</sub> + violuric acid	85
5-3	<u>1b</u> + H <sub>2</sub> O <sub>2</sub> + methyl syringate	89

10

**Example 6:**

Decolorization of **Remazol Brilliant Red 3BS** at pH = 8.3 and 25°C after various times

15

Example	Components in oxidizing system	Absorbance in % after t =			
		3 min	5 min	10 min	30 min
Comparison	<u>1b</u> + H <sub>2</sub> O <sub>2</sub>	3%	4%	7%	11%
6-1	<u>1b</u> + H <sub>2</sub> O <sub>2</sub> + HOBT	58%	77%	89%	97%

**Example 7:**

Decolorization of **Remazol Brilliant Red 3BS** at pH = 8.3 and 50°C after various times

5

Example	Components in oxidizing system	Absorbance in % after t =			
		3 min	5 min	10 min	30 min
Comparison	<u>1b</u> + H <sub>2</sub> O <sub>2</sub>	6%	9%	10%	11%
7-1	<u>1b</u> + H <sub>2</sub> O <sub>2</sub> + HOBT	96%	98%	98%	98%

**Examples 8**

The examples hereinbelow describe the use of the oxidizing system according to the invention in a preferred application, the decolorization of rinse liquors following a textile dyeing in the presence of the dyed textile.

The fabric used is a scoured and bleached cotton formed-loop knit which is dyed in a laboratory dyeing machine (a Mathis Spectradye for example) at a liquor ratio of 10:1 using the following recipe:

10 g of cotton are pretreated in a liquor consisting of

0.4 g/l of RESPUMIT® NF  
0.5 g/l of PERSOFTAL® L and  
55 g/l of sodium chloride

at 25°C for 10 minutes. The temperature is raised to 30°C, when

4% on weight of fiber of LEVAFIX® Brilliant Red E-RN

is added in 2 portions after 10 and 20 minutes, respectively. This is followed by the addition of

9.5 g/l of sodium carbonate

in three portions at intervals of 5 minutes in each case. After heating to 60°C at 1°C/min, the fabric is finally treated at 60°C for 60 minutes.

- 5 Immediately following the dyeing, the dyed cotton knit is rinsed in a liquor ratio of 10:1 as follows:

- (1) drop the dyeing liquor
- 10 (2) add fresh water, rinse at 60°C for 10 minutes, drop the liquor
- (3) add fresh water, rinse at 95°C for 10 minutes, drop the liquor
- (4) add fresh water, rinse at 90°C for 10 minutes, drop the liquor
- 15 (5) add fresh water together with
  - 1  $\mu$ M of compound **1b** and
  - 20 - 130  $\mu$ M of 1-hydroxybenzotriazole (HOBT)
  - treat at 60°C for 5 minutes, add
  - 4.4 mM of hydrogen peroxide
  - 25 treat at 60°C for 10 minutes, drop the liquor
- (6) add fresh water, rinse at 40°C for 10 minutes, drop the liquor and
- 30 (7) centrifuge and dry the cotton knit.

A comparative test is performed without addition of HOBT in the 5th rinse step. Otherwise all the steps are carried out in the same way.

The table below shows the coloredness of the individual rinse liquors (determined as absorbance E at 550 nm; the lower the absorbance, the lower the coloredness:

E at 550 nm	Inventive process	Comparative test - without HOBT -
1st rinse step	ca. 13	ca. 13
2nd rinse step	ca. 9.5	ca. 9.5
3rd rinse step	ca. 3.8	ca. 3.8
4th rinse step	0.18	1.23
5th rinse step	0.02	0.29

- 5 The results clearly show the significantly better decolorization of the rinse liquor in bath 4 in the presence of HOBT and the attendant lower coloredness of the last rinse liquor for the inventive process.

- 10 The wash-off effect is evaluated by determining the water fastness of the dyeing in accordance with German standard specification DIN 54006 (water fastness of dyeings, severe exposure). Cotton is used as adjacent fabric. The evaluation scale goes from 1 to 5, where 5 denotes the best fastness.

	Inventive process	Comparative test without HOBT
Rating	3-4	2-3

- 15 The inventive process accordingly provides a water fastness which is distinctly improved, namely by one rating point.

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☒ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**